QUALITY ASSURANCE PROJECT PLAN
SPARROWS POINT TERMINAL SITE
SPARROWS POINT, MD

Prepared for:

Prepared By:

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and

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ARM Project 150241

Revision 3

April 5, 2016

Executive Summary
Quality Assurance Project Plan
Sparrows Point Terminal Site

EnviroAnalytics Group (EAG) has requested that ARM Group Inc. (ARM) and Environmental Data Quality, Inc. (EDQI) prepare a Quality Assurance Project Plan (QAPP) to govern the work to be performed in compliance with the Administrative Consent Order (ACO) between Sparrows Point Terminal, LLC (SPT) and the Maryland Department of the Environment (MDE and the Settlement Agreement and Covenant Not to Sue (SA) between SPT and the United States Environmental Protection Agency (USEPA). The Agencies required the submittal of an updated QAPP to be uniformly implemented (i.e., a Generic QAPP) for the work to be performed by multiple consultants performing investigations.

A generic QAPP provides an overarching plan that describes the quality objectives and documents a comprehensive set of sampling, analysis, QA/QC, data review, and assessment procedures specific to a large program or long-term project. In contrast to the project specific QAPP, the generic QAPP serves as an umbrella under which multiple data collection, production and use activities may be conducted over an extended period of time.

The Agencies indicated that the QAPP should follow the EPA Guidance on Quality Assurance Project Plans (CIO 2106-G-05 QAPP). This QAPP utilizes the format of the Optimized UFP-QAPP Workbook, Revision 1, developed to facilitate the implementation of CIO 2106-G-05 QAPP. The UFP-QAPP Workbook, Revision 1 is a tool to guide project teams through the systematic planning process.

An approved generic QAPP should be supported by task or project specific addenda, which address the issues unique to each task or project. Project or task specific information that is not covered by the generic QAPP should be documented in detail in these addenda.

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APPENDICIES

LIST OF ACRONYMS

ACO	Administrative Consent Order
AOC	Area of Concern
ARM	ARM Group, Inc.
BSC	Bethlehem Steel Corporation
COPI	Chemicals of Potential Interest
DCQAP	Data Collection Quality Assurance Plan
DQOs	Data Quality Objectives
EAG	Enviroanalytics Group
EDQI	Environmental Data Quality, Inc.
EPA/USEPA	Environmental Protection Agency
MDE	Maryland Department of the Environment
MS	Matrix Spike
MSD	Matrix Spike Duplicate
µg/l	Micrograms per liter
OVM	Organic Vapor Monitor
%R	Percent Recovery
PCB	Polychlorinated biphenyl
PPA	Prospective Purchaser Agreement
QA	Quality Assurance
QC	Quality Control
RFA	RCRA Facility Assessment
RPD	Relative Percent Difference
RSC	Release Site Characterization
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
SPT	Sparrows Point Terminal, LLC
SSA	Special Study Area
SVOCs	Semi-volatile Organic Compounds
SWMU	Solid Waste Management Unit

TAL	Target Analyte List
TCL	Target Compound List
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound

REFERENCES

U.S. EPA (2012). *U.S. Environmental Protection Agency Guidance on Quality Assurance Project Plans.* (CIO 2106-G-05 QAPP). Final Draft. January, 2012.

QAPP Worksheet #1 & 2: Title and Approval Page
(UFP-QAPP Manual Section 2.1)
(EPA 2106-G-05 Section 2.2.1)

1. **Project Identifying Information:**

   a. ***Site name****:* Sparrows Point Terminal Property
   b. ***Site location:*** 1430 Sparrows Point Boulevard and 5111 North Point Boulevard Sparrows Point, Baltimore County, Maryland
   c. ***Contract Documents:*** Administrative Consent Order (ACO) with the Maryland Department of the Environment and Prospective Purchaser Agreement (PPA) with Region III of the United States Environmental Protection Agency

2. **Lead Organizations:** Sparrows Point Terminal, LLC (SPT) & Environmental Analytics Group (EAG)

   a. ***SPT Project Coordinator:*** Michael Pedone, COO

   _____ _____
   Signature Date

   b. ***EAG Project Manager:*** James Calenda, Project Manager

   _____ _____
   Signature Date

   c. ***EAG Quality Manager:*** Russell Becker, President

   _____ _____
   Signature Date

3. **Federal Regulatory Agency:** United States Environmental Protection Agency (USEPA) – Region 3

   a. ***USEPA Project Manager*****:** Andrew Fan, Project Manager

   _____ _____
   Signature Date

4. **State Regulatory Agency**: Maryland Department of the Environment (MDE)

   a. ***MDE Project Coordinator*:** Barbara H. Brown

   _____ _____
   Signature Date

5. **Primary Consultants:** ARM Group Inc. (ARM), Key Environmental, Inc. (KEY), and Environmental Data Quality, Inc. (EDQI)

   a. ***ARM Project Manager:*** Eric Magdar, Senior Geologist

   _____ _____
   Signature Date

   b. ***KEY Project Manager:*** Alan E. Briggs, P.E., Supervising Engineer

   _____ _____
   Signature Date

   d. ***EDQI Project Manager/Project Chemist:*** Shawne M. Rodgers, President

   _____ _____
   Signature Date

6. **Additional Consultants:**

   a. ***Project Manager:***

   _____ _____
   Signature Date

   b. ***Project Manager:***

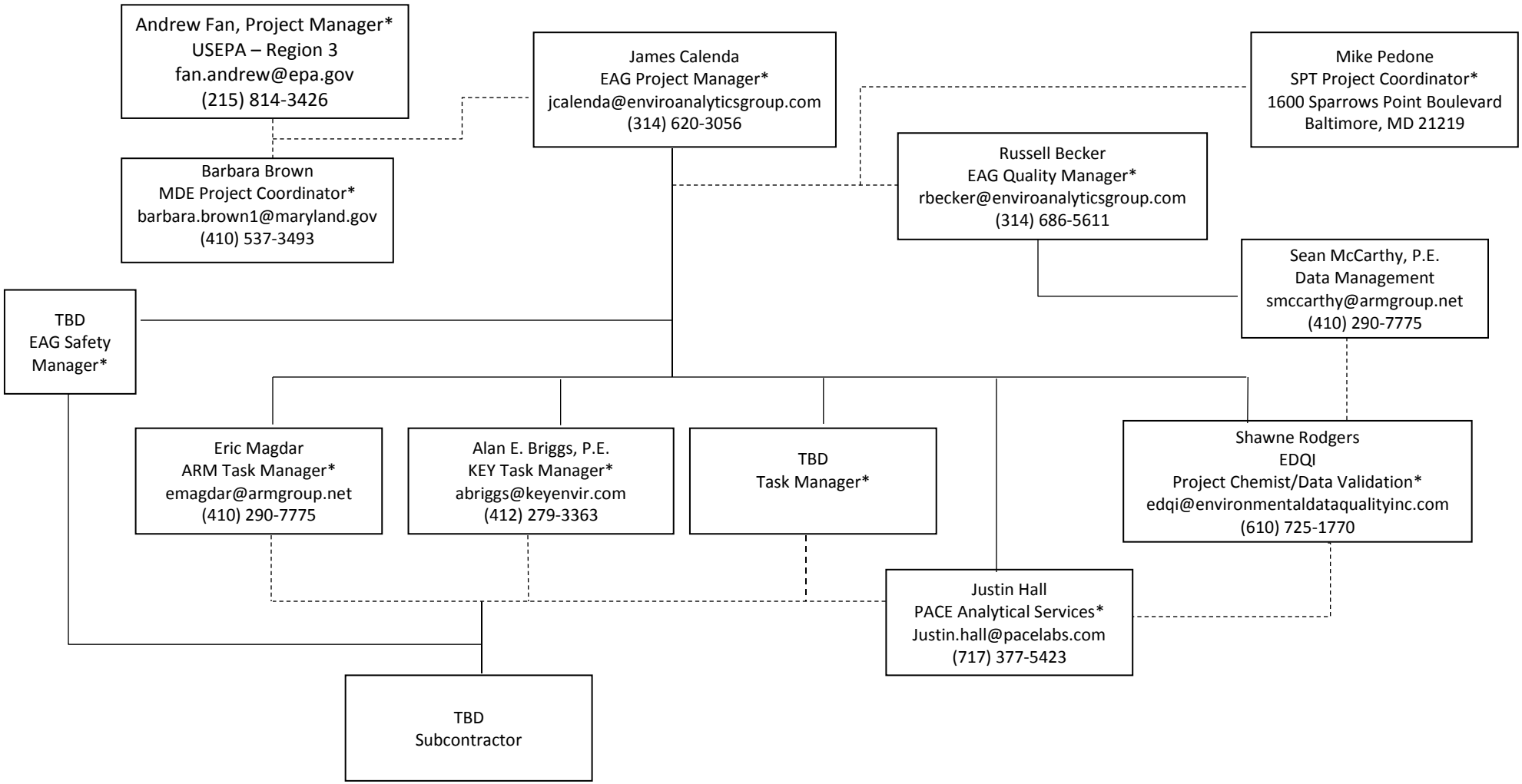
   _____ _____
   Signature Date

7. ***Relevant Reports and Plans:***

   a. Site Conceptual Cleanup Plan – Former RG Steel Facility, Sparrows Point Maryland , (EAG, August 2014)

QAPP Worksheet #3 & 5: Project Organization and QAPP Distribution
(UFP-QAPP Manual Section 2.3 and 2.4)
(EPA 2106-G-05 Section 2.2.3 and 2.2.4)

*QAPP recipient Lines of authority _____ Lines of Communication ----------



QAPP Worksheet #4, 7 & 8: Personnel Qualifications and Sign-off Sheet
(UFP-QAPP Manual Sections 2.3.2 – 2.3.4)
(EPA 2106-G-05 Section 2.2.1 and 2.2.7)

ORGANIZATION: EAG

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
James Calenda	Project Manager	B.S. Environmental Policy, St. Vincent College, 2007 8 years of environmental experience		
Russell Becker	Quality Manager	M.S. Geology, Tulsa University, B.S. Geology, Lehigh University, 30 years of environmental experience		

ORGANIZATION: ARM

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
Eric Magdar	Task Manager	B.S. Geology, Alfred University 1997 / 18 years of experience		
Sean McCarthy	Data Management	B.S. Civil Engineering, Bucknell University, 2004/ 9 years of experience	Professional Engineer	

ORGANIZATION: KEY

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
Alan E. Briggs	Task Manager	M.S., Civil Engineering, 34 years of experience	Professional Engineer	

ORGANIZATION: EDQI

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
Shawne Rodgers	Project Chemist/ Data Validation	B.S., Chemistry University of Pittsburgh, 1986		

ORGANIZATION: PACE ANALYTICAL

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
Justin Hall	Lab Coordinator	B.S., Biology/ 15 years of experience		
Samantha Bayura	Task Manager	B.S., Secondary Education Biology		

*Signatures indicate personnel have read and agree to implement this QAPP as written

QAPP Worksheet #6: Communication Pathways
(UFP-QAPP Manual Section 2.4.2)
(EPA 2106-G-05 Section 2.2.4)

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Regulatory agency interface	EAG	James Calenda	(314) 620-3056	Per project schedule or as needed. Minutes or notes should be maintained and distributed to regulator(s) and EAG.
Field progress reports	EAG/ARM/KEY/ Consultants	James Calenda/Task Managers	See Org Chart	During field activities, field personnel shall fill out daily field logs. Consultant Task Managers shall report to EAG Project Manager, at a minimum, on a weekly basis. Monthly reports will be provided to MDE and USEPA during field activities
Stop work due to safety issues	EAG/ARM/KEY/ Consultants	James Calenda/Task Managers	See Org Chart	Task Manager shall immediately report any safety issues to EAG Project Manager. Task Manager and EAG Project Manager shall refer to Health and Safety Plans associated with specific task. Incident Report shall be filled out.
QAPP changes prior to field work	ARM/EAG	Sean McCarthy	(410) 290-7775	Modify the QAPP as needed. Submit revision to MDE/USEPA. Distribute approved modifications as necessary.
QAPP changes during project execution	ARM/EAG	Sean McCarthy/ Russell Becker	(410) 290-7775/ (314) 686-5611	Discuss Modification with USEPA Manager. Determine if modifications merit work stoppage. Follow procedure above.

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Field corrective actions	EAG/ARM/ARC/KEY	Russell Becker	(314) 686-5611	Each Consultant Task Manager shall conduct audits of field collection procedures at the start of each sample collection of each investigation. An audit report shall be prepared and presented to EAG Project Manager
Sample receipt variances	PACE	Justin Hall	(717) 377-5423	PACE shall immediately notify EAG Project Manager of variance and inform him of personnel on COC. EAG shall notify appropriate Task Manager and determine the necessary corrective action.
Laboratory quality control variances	EDQI	Shawne Rodgers	(610) 725-1770	Notify laboratory immediately. Determine appropriate corrective action.
Analytical corrective actions	PACE	Justin Hall	(717) 377-5423	Per Laboratory QA/QC Manual. Laboratory Manager shall notify EAG immediately of any impacts to project data.
Data verification issues, e.g., incomplete records	EDQI	Shawne Rodgers	(610) 725-1770	Notify laboratory and other personnel involved in record keeping. If issues cannot be resolved. Determine if data is useable.
Data validation issues, e.g., non-compliance with procedures	EDQI	Shawne Rodgers	(610) 725-1770	
Data review corrective actions	EDQI	Shawne Rodgers	(610) 725-1770	

QAPP Worksheet #10: Conceptual Site Model
(UFP-QAPP Manual Section 2.5.2)
(EPA 2106-G-05 Section 2.2.5)

This worksheet presents the project's conceptual site model (CSM). The CSM is a tool to assist in the development of Data Quality Objectives (DQOs). The DQO process is described in Guidance on Systematic Planning Using the Data Quality Objectives Process (USEPA 2006). DQOs are revised as appropriate based on an improved understanding of the site to facilitate a more efficient and accurate characterization of the site and, therefore, achieve reductions in time and cost.

- **Background Information**

The "Sparrows Point Facility," in Baltimore County, Maryland comprises a 3,100-acre peninsula generally bounded by the Back River, Bear Creek, and the Northwest Branch of the Patapsco River, hereinafter the Site. From the late 1800s until 2012, the production and manufacturing of steel was conducted at Sparrows Point. Iron and steel production operations and processes at Sparrows Point included raw material handling, coke production, sinter production, iron production, steel production, and semi-finished and finished product preparation. In 1970, Sparrows Point was the largest steel facility in the United States, producing hot and cold rolled sheets, coated materials, pipes, plates, and rod and wire. The steelmaking operations at the Facility ceased in fall 2012.

EPA and MDE have been overseeing investigations and interim remedial measures to address contamination at the Site since at least 1987 and have received numerous reports regarding the scope of Waste Material at the Site, including but not limited to:

- Description of Current Conditions (Rust 1998)
- Site-Wide Investigation Work Plan- Groundwater Study (CH2M Hill 2000)
- Site-Wide Investigation Groundwater Study Report, July 2001 (CH2M Hill 2001)
- Site-Wide Investigation Release Site Characterization Study, June 2002 (CH2M Hill 2002)
- Site-Wide Investigation: Report of Nature & Extent of Releases to Groundwater From the Special Study Areas (URS 2005), revised 2007
- CA725 Facility Investigation and Human Health Risk Evaluation (HHRE) Findings, ISG Sparrows Point, June 2005 (URS 2005)
- Ecological Risk Assessment Strategy Document; ISG Sparrows Point Facility (URS 2006)
- Final Ecological Risk Assessment Work Plan for On-Site Areas (URS 2007)
- Screening Level Ecological Risk Assessment For On-Site Areas Final (URS April 2009)
- Final Baseline Ecological Risk Assessment for On-Site Areas (BERA) Report (URS 2011).
- Phase I Assessment of the Site (Weaver Boos May 20, 2014).
- Draft Site Conceptual Cleanup Plan (SCCP) (EAG May 22, 2014).

Sparrows Point Terminal, LLC (SPT) purchased the property on December 14, 2013 and plans to redevelop the Site into a transportation, manufacturing, and logistics industrial campus. Environmental responses for the site in general, are being implemented pursuant to the following:

- Administrative Consent Order (ACO) between SPT and the Maryland Department of the Environment (effective September 12, 2014);
- Settlement Agreement and Covenant Not to Sue (SA) between SPT and the United States Environmental Protection Agency (effective November 25, 2014).

On October 8, 1997, Bethlehem Steel Corporation (BSC) entered into the BSC Consent Decree with the United States of America and the State pursuant to RCRA, among other federal authorities, and the Environment Article of the Annotated Code of Maryland. The BSC Consent Decree sets forth a summary of conditions at the Property, and requires characterization of the impact of releases at and from the Property, in a SWI; completion of a CMS; and (if required by EPA and/or MDE) implementation of IMs to address contamination. Pursuant to the BSC Consent Decree, BSC was required to, among other things, perform Interim Measures (IMs), a Site Wide Investigation (SWI), and a Corrective Measures Study (CMS).

BSC and subsequent owners of the Property have completed much of the SWI and implemented certain EPA-required IMs, including groundwater extraction at the former Rod and Wire Mill and installation and operation of groundwater extraction treatment Cells 1 - 6 in the Coke Oven Area. On July 28, 2014, the federal District Court for Maryland entered an amendment to the BSC Consent Decree which added Sparrows Point LLC (SPLLC), the current owner at that time, as a Respondent, acknowledged that certain work required under the BSC Consent Decree had been completed, and clarified certain other provisions. As a result, SPLLC is currently responsible for carrying out the terms of the Consent Decree related to the Site.

The original BSC Consent Decree for the Sparrows Point facility dealt with many issues associated with ongoing iron-making, steel-making, coking, byproduct, plating, and finishing operations. To the extent that these operations are no longer conducted, and the associated facilities no longer exist, many specific requirements of the Decree are no longer applicable and have been removed in accordance with the stipulated order implementing modifications to the Decree. In addition, approximately 2200 acres of the Property have been designated as Carve Out Areas and removed from the jurisdiction of the BSC Consent Decree and no further investigation or corrective measures will be required under the terms of the BSC Consent Decree for the Carve Out Areas. The property within the Carve Out Area will remain subject to the RCRA Corrective Action authorities, in accordance with RCRA and the SA. The aforementioned ACO and SA incorporate the relevant aspects of the BSC Consent Decree by reference.

- **Key physical aspects of the site (e.g., site geology, hydrology, topography, climate)**

The Sparrows Point Site is bordered by water on three sides with land connection predominantly to the north and northeast. The peninsula is bounded to the east by Old Road Bay and Jones Creek; to the south by the Patapsco River; and to the west by Bear Creek, all of which directly or indirectly drain to the Chesapeake Bay located southeast of the Site. The original topography of the peninsula was flat with elevations not exceeding 15 feet North American Vertical Datum 1988 (NAVD88). The peninsula has been drastically altered since the inception of the steel manufacturing activities. Creeks have been filled in and new land has been added to various areas of the Site by building up near-shore areas of the river.

The current ground surface at the Sparrows Point Site is relatively flat. All major topographic features (such as buildings, landfills, and material stockpiles) are manmade. Throughout most of the peninsula, the elevation of the ground surface is between 0 and 20 feet mean sea level (msl). The average elevation is about 15 feet msl. In the southern portion of the Site, there are several manmade landforms (raw and byproduct material stockpiles) that exceed 20 feet msl in elevation. Greys Landfill, located near the northwestern corner of the property, is approximately 110 feet msl in elevation at its highest point.

Surface water runoff is diverted and collected by a network of culverts, underground pipes, and drainage ditches within the Site. The stormwater is then discharged to Bear Creek, Jones Creek/Old Road Bay, and the Patapsco River. Prior to 1970, much of the stormwater from the northern part of the Site was discharged to Humphrey Creek and subsequently to Bear Creek. Between 1950 and 1970, the Tin Mill Canal was constructed within portions of Humphrey Creek which continued to receive stormwater from the northern part of the Site. Since about 1970, stormwater runoff from the northern part of the Site has discharged to the Tin Mill Canal, and then conveyed to the Humphrey Creek Wastewater Treatment Plant (HCWWTP) for treatment.

- **Land use considerations**

Zoning maps indicate that the Sparrows Point Site is zoned Manufacturing Heavy - Industrial, Major (MH-IM). Surrounding property zoning classifications include the following: Manufacturing Light (ML), Resource Conservation (RC), Density Residential (DR), Business Roadside (BR), Business Major (BM), Business Local (BL), and Residential Office (RO). The Sparrows Point Country Club is located north of the Sparrows Point Site on the other side of the Peninsula Expressway. Light industrial and commercial properties are located northeast of the Site and northwest of the Site on the other side of Bear Creek. Residential areas of Edgemere and Fort Howard are located northeast of the Site and east of the Site on the other side of Jones Creek and Old Road Bay. Residential areas of Dundalk are located northwest of the Site on the other side of Bear Creek.

SPT plans to redevelop the Site into a transportation, manufacturing, and logistics industrial campus. Efforts will be completed to return the entire Site to “market ready” conditions and to complete

response actions for select areas of the Site in an effort to return these areas to productive use. Site-wide institutional and legal controls will be established and integrated within the response actions. These controls are anticipated to include, but will not necessarily be limited to, the following:

- Deed restriction for commercial/industrial site use only, no portion of the Site will be used for agricultural, recreational or residential purposes
- Deed restriction on groundwater use, no subsurface water or groundwater will be extracted from aquifers for any purpose
- Development and implementation of soil/materials management plans for remedial and redevelopment activities
- Where necessary, restriction on development/reuse or use of vapor intrusion control technologies for occupied buildings

- **Sources of Known or Suspected Hazardous Waste;**

Based upon a 1994 RCRA Facility Assessment and a 1998 Description of Current Conditions Report, EPA and MDE determined that further investigation and/or action was needed at 81 solid waste management units (SWMUs) and 28 areas of concern at the Property. The BSC Consent Decree organized these SWMUs and Areas of Concern into five (5) designated "Special Study Areas (SSAs)" to be focused upon during RCRA Corrective Action activities: the Tin Mill Canal/Finishing Mills, Greys Landfill, Humphreys Impoundment, Coke Point Landfill, and the Coke Oven Areas. The Coke Point Landfill and the Coke Oven Areas are located on the Coke Point peninsula on the Property.

The Phase I Assessment of the Site (Weaver Boos May 20, 2014) identifies potential hazardous waste sources in addition to the sources already identified in the five SSAs. These potential sources were identified as findings or Recognized Environmental Conditions (RECs) through review of historical operations, inspection of historical aerial photographs, and site inspections. In most cases, there has been no prior investigation and it is not known whether there have been releases to the environment associated with the potential sources identified in the Phase I report.

Historical plant drawings have been digitized and geo-referenced into a GIS database to identify the locations of plant activities that may be sources of releases of petroleum or hazardous substances. These site drawings included the 5000 Set (Plant Arrangement), the 5100 Set (Plant Index), the 5500 Set (Plant Sewer Lines), and a set of drawings indicating coke oven gas distribution drip leg locations. These plant drawings have been used to identify potential sources of releases of petroleum or hazardous substances, including motor rooms, scale pits or handling areas, pump houses, fuel storage, other storage tanks, lube shops or rooms, soaking or other pits, sumps, trenches, process shops, furnaces, drip legs, settle basins, transformer storage areas, machine rooms, shears, and coal bins.

- **Known or Suspected Contaminants or Classes of Contaminants;**

Historic SWI studies have found elevated levels of a broad range of contaminants at the Site including: antimony, arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, tin, zinc, ammonia, benzene, cyanide, ethyl benzene, ethylene glycol, hydrogen cyanide, hydrogen sulfide, naphthalene, polycyclic aromatic hydrocarbons (PAHs), PCBs, pentachlorophenol, phenols, pyrene, sodium phenolate, styrene, sulfuric acid, toluene, trichloroethylene, xylene, coal tar, other volatile organic carbons (VOCs), oils, lime sludge, waste alkaline rinses, and mill scale. SWI studies indicate that the most contaminated portions of the Site are located at the Coke Point peninsula. Organic compounds, in particular benzene and naphthalene, have been identified in SWI studies as the primary constituents of concern in groundwater on the Property.

- **Primary Release Mechanism(s)**

The historical primary release mechanisms consist of:

- direct discharge of wastewater into impoundments or canals
- direct placement of solid wastes into/onto soils
- spills or leaks from process operations or facilities

- **Secondary contaminant migration**

Possible migration pathways may include:

- transport of contaminants by mechanical disturbance (e.g. excavation).
- leaching of contaminants through the soil profile to groundwater
- downward migration from one groundwater aquifer to another
- transport of contaminants via groundwater to surface water
- transport of contaminants via stormwater to surface water, and
- volatilization from soil and/or groundwater to air (indoor and outdoor).

- **Fate and transport considerations**

Previous groundwater studies have demonstrated that shallow groundwater flow is from the upland areas toward the surrounding, tidally influenced surface water bodies (i.e., Patapsco River/ Bear Creek, and the Turning Basin).

From a geochemical standpoint, the most significant issue is the elevated pH of the shallow groundwater in portions of the site. A large portion of the Site is “made land” resulting from the placement of iron and steel-making slag. The fluxing agent for iron-making is typically limestone or dolomite and the fluxing agent for steel-making is typically lime. The use of these materials results in slags with water soluble calcium and magnesium oxides which react with water to result in alkaline conditions (the pH of water in equilibrium with iron and steel-making slags can range as high as 11.5 to 12.5 SU).

The primary implication of this geochemical consideration is biological in nature. Specifically, benzene, toluene, ethylbenzene, xylenes and other aromatic hydrocarbons are typically recognized to be biodegradable under aerobic (and anaerobic) conditions. Groundwater plumes consisting of these constituents are generally attenuated as a result of sorption, hydrodynamic dispersion, diffusion, and biodegradation. As a result of the elevated pH in the shallow water bearing zone in the Coke Oven Area, biodegradation appears to be a negligible component of natural attenuation for the dissolved constituents in groundwater. In addition, the slag matrix is essentially a glasslike material which is expected to be very low in organic carbon content. Hence, in addition to inhibition of biological processes, the slag may offer very limited sorption potential for dissolved phase constituents.

By contrast, the pH of the groundwater in the intermediate zone is near neutral and hence the potential for biological degradation of dissolved phase constituents in the intermediate zone is not inhibited. In addition, the intermediate groundwater zone also consists of native materials such as former open water sediments or marsh deposits that are likely to exhibit higher levels of organic carbon and hence greater sorption potential.

- **Potential receptors and exposure pathways**

Access to the Site is currently limited to workers only. The site is fenced with 24-hour security provided. As discussed, SPT is in the process of redeveloping the Site into a transportation, manufacturing, and logistics industrial campus. As such, future use of the Site will be subject to institutional controls that will limit potential receptors and exposure pathways. In addition, the development plans will include construction of buildings and paving of areas that will prevent contact with subsurface materials in large areas of the Site. Therefore, future exposure to impacted material are expected to be limited, with the primary potential pathways for exposure being limited exposure to surface soils for commercial workers and site visitors, discharge of groundwater constituents to surface waters, and exposure to indoor air potentially impacted by volatilization of constituents from impacted subsurface soils and groundwater.

- **Current Interpretation of Nature and Extent of Contamination**

As noted in the ACO and SA, several prior owners of the Property have completed much of the SWI for the Property. Much of the investigation has been focused on the Special Study Areas where impacts have been identified. However, additional delineation and characterization in these areas is still needed to gather the data needed to support the selection and design of appropriate remedial measures.

The Carve-Out Areas include a mix of manufacturing and support operations where petroleum products and hazardous materials were utilized as well as open areas where little historic industrial activity took place, but these areas were not identified in previous studies as containing large solid or hazardous waste management units requiring investigation. As a result, there are not large known areas of contamination within these areas. Phase I investigations have identified specific Recognized Environmental Concerns for further investigation as potential sources of releases to the environment.

- **Data gaps and uncertainties**

The purpose of future site characterization is to identify any existing hazardous conditions across the entire site, and in particular, the identified Recognized Environmental Conditions (RECs) provided in the Phase I Environmental Site Assessment (ESA) prepared by Weaver Boos Consultants dated May 19, 2014. Data gaps and uncertainties to be addressed by further site assessments and pre-design investigations include the following:

- Delineation and characterization of impacts to soil and groundwater in the SSAs
- Determination of the presence or absence of Areas of Concern (AOCs) within the Carve-out Area

QAPP Worksheet #11: Project/Data Quality Objectives
(UFP-QAPP Manual Section 2.6.1)
(EPA 2106-G-05 Section 2.2.6)

Data Quality Objectives (DQOs) specify the appropriate quantity and type of data required to make informed environmental and risk management decisions, including tolerable levels of uncertainty. USEPA has developed a systematic process for developing DQOs that includes consideration of several critical elements. The process requires definition of the problem and statement of the decisions that will be made based on the study results. Information needed to support the decision making process can then be defined, and includes identification of the constituents or parameters of interest, delineation of the physical boundaries of the study area, definition of the quantity of data that will be needed, identification of the means to collect the required data, and the level of uncertainty that will be acceptable. The objective of the DQO process is to develop a framework for addressing specific contamination problems and determine sampling designs that are intended to collect the right type, quantity, and quality of data to support decision making. Through the DQO process, the data collection programs can then be optimized to ensure the collection of defensible data in the most efficient manner.

- **Problem Statement**

This generic QAPP is intended to govern a wide range of investigations and monitoring being conducted during different phases from initial site assessment activities to evaluations of remedial operations at the Sparrows Point Facility in support of the remediation of the site in accordance with the requirements of the Maryland Voluntary Cleanup Program and the USEPA RCRA Corrective Action program. The problem is how to ensure that adequate data is collected to satisfy each task below:

1. Determine if TCL VOCs, SVOCs, PCBs, TAL metals, cyanide, DRO or GRO are present in site media at concentrations that could pose an unacceptable risk to site receptors. Individual results will be compared to the most current USEPA RSLs and MDE soil vapor Project Action Limits.
2. Evaluate potential risk to future on-site human and ecological receptor populations under the planned future industrial use scenario. This evaluation may be tiered, with an initial screening based upon the RSL standard industrial exposure parameters. This initial screening will be used to identify those portions of the site requiring additional evaluation and/or remediation, and also define portions of the site that need no further

action.. If the initial screening indicates the need for further evaluation, the investigations may include quantitative risk assessment for all or portions of the site. If risk assessment is necessary, data will have to be sufficient to support 95% UCL exposure point concentrations. In addition, large parcels would have to be broken up into multiple exposure units, each with adequate data (at least an N of 10). A risk ratio approach in lieu of a site-specific risk assessment may also be used with acceptance of the RSL standard industrial exposure parameters.

3. Identify and delineate the media requiring remediation, based on the results of the risk evaluation.
4. Support the selection and design of appropriate remedies and preparation of Response Action Plans,
5. Monitor the progress of remedial activities through analysis of soil and groundwater concentrations, well gauging, periodic well samples, etc.
6. Monitor and ensure compliance with State and federal rules and regulations during remedial activities through discharge monitoring, breathing zone monitoring, waste characterization sampling, etc.
7. Confirmation sampling to demonstrate attainment of the remedial action objectives.

While the investigations covered by this QAPP will be limited to the on-shore portions of the Sparrows Point Facility, the data collected during these investigations may also be used to support the USEPA's assessment of risk in the off-shore areas adjacent to the facility.

- **Decision Goals**

Decisions that will be based on the data generated during the investigations governed by this generic QAPP at various stages in the remediation process will include:

1. *Risk Evaluation*

    a. Risk Screening - Has a release of hazardous constituents that poses a potential threat to human health or the environment occurred (i.e., are exceedances of the USEPA RSLs and MDE soil vapor PALs observed in sample results)?
    b. Tier I Risk Ratio Evaluation – Does the site contamination pose a potential unacceptable risk to on-site human and ecological receptors under the planned industrial use development scenario (i.e., does the risk ratio approach indicate a potential for unacceptable cancer or non-cancer risk using the RSL standard industrial exposure parameters)?

c. Tier II Risk Assessment - Does the site contamination pose an unacceptable risk to on-site human and ecological receptors under the planned industrial use development scenario (i.e., does risk assessment indicate that the site contamination presents a cumulative excess lifetime cancer risk of greater than $1x10^{-5}$ or a non-cancer hazard quotient greater than 1.0)?
d. What is the distribution of contaminants that exceed the RSLs or MDE soil vapor PALs, or drive the exposure point concentration causing an unacceptable risk?
e. Are specific parcels acceptable for use while further investigation and remediation activities continue?
f. Are residual on-site concentrations serving as continuing sources of contamination to off-shore areas?

2. *Assessment of Remedial Alternatives and Operations*

a. What remedial alternatives are technically practicable for on-site areas that present an unacceptable risk or that serve as a continuing source of contamination to off-shore areas?
b. Are the selected remedial technologies performing at a level (i.e., removal rates, decreasing influent concentrations, decreasing product thicknesses, decreasing monitoring well concentrations, etc.) that will ensure remedial objectives are met?

3. *Cleanup Attainment Evaluations*

a. Has the final remediation level been achieved?

- **Information Inputs to Decisions**

The proposed investigations will gather a variety of information required to support the decision making process. This will include representative constituent concentrations in various media in various portions of the site. The investigations will characterize concentrations in surface soil, subsurface soil, groundwater and soil gas in the planned redevelopment areas, as well as sediments and surface water in on-shore water bodies.

Surface soil will be characterized by samples collected from the top 1 ft. Subsurface soil at depths of 1 ft to 10 ft below ground surface (bgs) will be characterized by sampling at intervals of 4-5 ft bgs and 9-10 ft bgs. Groundwater quality will be characterized through the installation

and sampling of wells in the shallow and intermediate flow zones. Sub-slab soil gas concentrations will be characterized in existing buildings that are proposed for re-use,. In the event that soil or groundwater data indicate a potential for unacceptable vapor intrusion into future buildings where existing slabs are not present, soil gas samples will be collected from a depth of 10 ft, or 2 ft above the water table if present at a depth of 10 ft or less. On-site sediments will be characterized by samples from the top 1 ft and at deeper depths as required to assess remedial alternatives and on-site surface water will be characterized by collection of depth-discrete samples at mid-column depth.

While previous investigations have been performed in portions of the site **(the Corrective Action Areas)** that have identified the constituents of potential interest (COPIs) for these areas, other areas **(the Carve-Out Areas)** have not yet been fully investigated **(see Figure 1)**. Therefore, initial investigations in **the Carve-Out** will gather data for a wide range of potential constituents to ensure that all COPIs are identified for each portion of the site and each environmental medium. The analyses performed in the initial investigations will include the USEPA Target Compound List (TCL) of volatile and semivolatile organic compounds, the USEPA Target Analyte List (TAL) of metals and cyanide, hexavalent chromium, total petroleum hydrocarbons (gasoline and diesel range), polychlorinated biphenyls (PCBs), and oil and grease.

The investigations will also improve the understanding of the geologic and hydrologic characteristics of the study area. This information will be used to define contaminant migration and to estimate exposure point concentrations that will be used in conjunction with USEPA RSLs and MDE soil vapor PALs for the purposes of screening level risk evaluation. This information may also be used in support of site-specific risk assessments to develop quantitative cumulative risk estimates that assess risk to on-site receptors. In addition and as applicable, the on-site concentrations and contaminant migration parameters defined during these investigations will be used to assess potential contributions to continuing contamination and risk in off-shore areas.

Information collected regarding the distribution and characteristics of contamination identified on the site, along with characteristics of subsurface matrix and the hydrogeology, will be used to identify and evaluate the applicability and effectiveness of potential remedial approaches and technologies. Monitoring of remedial operation influents and effluents will be used to evaluate regulatory compliance, and confirmatory samples will be collected to assess achievement of remedial goals.

- **Boundaries of the Study**

The study area includes the on-shore portions of the Sparrows Point property, comprising a 3,100-acre peninsula generally bounded by the Back River, Bear Creek, and the Northwest Branch of the Patapsco River. The media of concern will include surface and subsurface soil, groundwater and soil gas in areas to be developed, and sediment and surface water in on-shore water bodies. Many of the **Corrective Action Area** SWMUs have been subject to prior investigations that have identified a list of COPIs for these units. However, other areas **(Carve-Out Areas)** have yet to be fully investigated. Therefore, initial investigations will include analysis for a wide range of constituents, including the USEPA Target Compound List (TCL) of volatile and semivolatile organic compounds, the USEPA Target Analyte List (TAL) of metals and cyanide, hexavalent chromium, total petroleum hydrocarbons (gasoline and diesel range), polychlorinated biphenyls (PCBs), and oil and grease. Work plans for subsequent investigations may focus on subsets of these constituents based on initial screening.

Redevelopment and reuse of the Sparrows Point property is anticipated to take place within the next two year timeframe, although groundwater use is to be restricted and investigation and remediation, if needed, has been segregated from site redevelopment to be completed on a parallel but potentially longer schedule. The Sparrows Point property has been subdivided into parcels which have been prioritized for evaluation and redevelopment. Therefore, the goal is to develop a sampling program that will allow for risk management decisions to be made on the suitability of individual parcels for reuse, while the investigation of other parcels, and the groundwater is on-going. The anticipated use of the site will be restricted to industrial so the focus of the study will be to assess the risk to future on-site workers and construction workers within the redeveloped areas. In addition, risk to ecological receptors will be evaluated for the areas of the site that will not be developed.

While the investigations under the QAPP will be limited to the on-shore Sparrows Point Facility, some of the data collected during these investigations will be used along with off-shore data collected by others to assess potential continuing contributions to contamination and risk in off-shore areas.

- **Decision Rules**

1) If the collected data are found to be acceptable through the qualitative and quantitative comparisons to acceptance criteria (primarily Worksheet 12 and supporting worksheets) and adequately representative of a given parcel (primarily Worksheets 17-18, and supporting worksheets), then the project decisions below can be made.

If screening of sample results within a parcel (decision unit) indicate the upper-bound estimates of the mean concentrations exceed the Project Action Levels (PALs), then assessment of risk will be conducted, or remedial measures will be implemented to mitigate the identified potential risk. PALs are the most current published USEPA Regional Screening Levels (RSLs) for soil or water or the MDE soil vapor screening criteria, as indicated in Worksheet #15. Measurement detection and quantitation limits for laboratory analytical methods must be low enough for quantitative comparison with the applicable RSL or MDE value for all key constituents of potential concern (Worksheet #15). Risk management decisions on the use of the land may be made independently for individual parcels, while the investigation and remediation of other areas, or the groundwater is ongoing. If the contaminant concentrations are below the PALs, then no further action would be warranted for that decision unit.

2) If the upper-bound estimate of the cumulative excess lifetime cancer risk to an on-site receptor exceeds $1x10^{-5}$, or the non-cancer hazard index exceeds 1.0 for any individual target organ, then remedial action will be implemented to mitigate the identified risk. Data gathered for the purposes of quantitative risk assessment must provide representative upper-bound estimates of the mean concentration of constituents in environmental media. If risk assessment is necessary, data will have to be sufficient to support estimation of 95% UCL exposure point concentrations and large areas would have to be broken up into multiple exposure units, each with adequate data (at least an N of 10).

3) If the residual contaminant concentrations for a decision unit are below the Cleanup Levels defined in the relevant Response Action Plan (RAP) for that unit, then remediation would be considered complete for that decision unit. Data for the purposes of attainment of remedial action objectives must be representative of the residual concentrations of the Constituents of Potential Interest established within the relevant RAP. These data will be used to determine when remediation is complete and therefore the measurement detection and quantitation limits must be consistent with the cleanup levels to be established within the RAP. Cleanup levels may be based on the applicable RSL or MDE value, or on risk-based values to be determined on a site-specific basis if warranted. Comparisons may be made based upon individual results not to exceed the cleanup levels, or based upon the 95% UCL of the mean value of the residual concentrations, depending on the method specified in the RAP.

- **Performance or Acceptance Criteria**

Data used for risk assessment and risk management decisions will be subjected to Stage IIB data validation. Worksheet #20 shows the field quality control (QC) samples required. Worksheets #12 and #28 show the measurement performance criteria for the quality indicators to ensure the usability of the data for risk management decisions.

The possibility of a decision error exists because the parameter of interest is estimated using data that are never perfect but are subject to different variabilities at different stages of development, from field collection to sample analysis. The combination of all these errors is called "total study error," and for sampling at potential remediation sites, this can be broken down into two main components:

(1) **Sampling design error**. This error (variability) is influenced by the sample collection design, the number of samples, and the actual variability of the population over space and time. It is impractical to sample every unit of the media, and limited sampling may miss some features of the natural variation of the contaminant concentration levels. Sampling design error occurs when the data collection design does not capture the complete variability within the media to the extent appropriate for the decision of interest.
(2) **Measurement error**. This error (variability) is influenced by imperfections in the measurement and analysis system. Random and systematic measurement errors are introduced in the measurement process during physical sample collection, sample handling, sample preparation, sample analysis, and data reduction.

In some cases, total study error may lead to a decision error. Therefore, it is essential to reduce total study error to a minimum by choice of sample design and measurement system in order to reduce the possibility of making a decision error.

The assumption for the purposes of the Phase II investigations, or for attainment of remedial objectives, is that the contaminated media contains concentrations in excess of the Project Action Limits (Worksheet #15). A biased sampling approach will be utilized to minimize the potential for falsely rejecting this assumption. Using the extensive records available on operations and activities on the site, sample locations will be biased toward the "target areas" where the highest levels of contaminants would be expected. This approach to sampling design will minimize the potential that the decision could be based on data that understates the true concentrations present in the media. In addition to the locating samples within "target areas" the sampling strategy includes site-wide sampling as a back-up system to failures of the biased sampling strategy. The potential for measurement error is minimized by the evaluation of

QA/QC samples including blind duplicates, blank samples, and spiked samples. The results of these samples will be reviewed during the data validation process to identify random measurement error or systematic bias.

Risk management decisions may also involve estimation of the 95% upper confidence limit on the mean values for the generation of risk and hazard estimates. In that case, the data set for each decision unit (parcel) must be sufficient to facilitate statistical analysis to develop a defensible upper bound estimate of mean exposure point concentrations within that unit.

- **Plan for Obtaining Data**

Since this QAPP is intended to govern a wide range of investigations, specific plans for obtaining data will be presented in work plans for specific tasks. As discussed above, there is a significant amount of information available on the past operation and activities at the site, as well as previous investigations in portions of the site. This historical information will be used to design sampling programs that are biased toward the target areas where the highest levels of contaminants would be expected. The approach to and rationale for sampling design for various potential investigations are discussed in Worksheet #17. The work will be conducted in accordance with the field standard operating procedures (SOPs) presented in Appendix A and the laboratory SOPs presented in Appendix B.

As a result of the varying nature of the data required for various decisions, there are several potentially applicable levels of data quality for the investigations. A primary component of data quality is selection of the appropriate analytical level for the intended data use. Analytical levels, as described in "Data Quality Objectives for Remedial Response Activities" (USEPA, March 1987), are as follows:

Level I:

Field screening or analysis using portable instruments. Results are often not compound-specific and not quantitative, but are available in real-time. Level I data are appropriate for initial field screening and for health and safety monitoring. They are frequently used to determine sample collection locations for laboratory analyses.

Level II:

Field analysis using more sophisticated portable analytical instruments; in some cases, the instruments may be set up in a mobile laboratory on location. There is a wide range in the quality of data that can be generated that is dependent on the use of suitable calibration

standards, reference materials and sample preparation equipment. Results are available in real-time or within several hours.

Level III:

All analyses are performed in an off-site analytical laboratory. Level III provides quantitative data. Documented sampling and analysis procedures must be used. Level III analyses may or may not use Contract Laboratory Program (CLP) procedures, but at a minimum, abbreviated CLP-type deliverables are required. Level III may require data validation and QA/QC procedures conducted in accordance with USEPA guidelines. The laboratory may or may not be a CLP laboratory.

Level IV:

CLP-equivalent routine analytical services. All analyses are performed in an off-site analytical laboratory following CLP protocols. Level IV is characterized by rigorous QA/QC protocols and documentation with full validation of all data.

Level V:

Analysis by nonstandard methods. All analyses are performed in an offsite laboratory that may or may not be a CLP laboratory. Method development or method modification may be required for specific constituents or detection limits. CLP Special Analytical Services (SAS) are Level V.

For the purposes of these investigations, the Analytical Levels to be employed consist of Levels I and IV. The Analytical Levels to be employed consist of the following:

- Level I – Field Instrumentation Measurements.
- Level IV – Contract Laboratory Program Equivalent Data.
- Level V – Analysis by nonstandard methods to support bench scale treatability work. Geotechnical Laboratory analyses.

As noted, work plans will be provided for each task. These work plans will rely upon the methods specified in this generic QAPP, but depending on the purpose and objectives of the specific study, will provide additional detail on the proposed field sampling plans, including the specific sampling design and rationale, the number of data points required, and the required analyte list.

QAPP Worksheet #12: Measurement Performance Criteria
(UFP-QAPP Manual Section 2.6.2)
(EPA 2106-G-05 Section 2.2.6)

Qualitative/Quantitative Comparisons to Acceptance Criteria

The DQIs of precision, accuracy/bias, representativeness, completeness, comparability, and sensitivity are described below:

Precision indicates the reproducibility of individual lab results on a single true sample. To increase precision, consistent sampling and analytical protocols will be followed. All work will adhere to the practices set forth in the QAPP. Precision checks will be performed by the inclusion of field duplicates. Quantitatively, the precision of the tests can be calculated using the Relative Percent Difference (RPD) equation:

RPD = (A-B) / C x 100
A = analytical result from one of two duplicate measurements
B = analytical result from second of two duplicate measurements
C = arithmetic mean of the two measurements A and B

Accuracy/Bias tells how close a measurement is to the true value. Calibrations of instruments at the throughout the testing process are used to monitor the accuracy of the tests. Reference control samples, matrix spikes, and blanks are used to assess the accuracy of data. Quantitatively, accuracy will be measured as below:

% Recovery = (A-C)/B x 100
A = value measured in spike or standard
B = true value of the standard or spike
C = value measured in original sample

Representativeness is a measure of how accurately and precisely the data describe the site conditions. This factor depends on variability in the sampling techniques and analytical results, as well as variability within the site environment (soil, groundwater, etc.). The QAPP describes the basis for sampling locations and quantities of sample gathered. Use of the prescribed field and laboratory methods, coupled with appropriate sample preservation, is intended to promote representativeness within the data.

Completeness is a DQI comparing the amount of valid data to the total amount of data that was gathered during a particular investigation. This value is determined following the completion of analytical results, based on the observed results. The completeness of the data is assessed by professional judgement and should be greater than or equal to 90%, as measured by the following formula:

Completeness = A/B x 100
A = number of valid analytical results for given investigation
B = total number of analytical results for given investigation

Comparability describes the degree of confidence in comparing two sets of data. Comparability is maintained across multiple datasets by the use of consistent sampling and analytical methods across multiple project phases. QA/QC protocols also maintain the comparability of datasets. Comparability is assured by the use of accepted practices, and data reporting will use standard units.

Sensitivity is a determination of whether the analytical methods and quantitation limits will satisfy the requirements of the project. Method quantitation limits are determined by the instrumentation and procedures in the laboratory, and set by in-house criteria. The laboratory quantitation limits for specific analytes are given in Worksheet #15.
Further information on the DQIs of accuracy/bias, precision, and sensitivity is located in Worksheet #28. A list of documents, records, and analytical results to be evaluated for completeness is located in Worksheet #34. The Pace Analytical Quality Assurance Manual, rev 17.2, revised 12/22/2014 describes further detail on laboratory specific DQIs.

Matrix: Air
Analytical Group or Method: VOCs/TO-15
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	RPD ≤ 30% when VOCs are detected in both samples ≥ sample-specific LOQ
Analytical Precision (laboratory)	Laboratory Duplicates Laboratory Control Sample Duplicates	RPD ≤ 25%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific
Overall Accuracy/Bias (contamination)	Laboratory Method Blanks	No target analyte concentrations ≥ LOQ
Sensitivity	LOQ verification sample (spiked at LOQ)	Recovery within ±25% of LOQ
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: VOCs/SW846 8260B
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when VOCs are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	LCS/LCSD MS/MSD	RPD ≤ 30% when VOCs are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Trip Blanks, Method Blanks & Instrument Blank	No target compound ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: SVOCs/SW846 8270D
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when SVOCs are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	LCS/LCSD MS/MSD	RPD ≤ 25% when SVOCs are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks & Instrument Blank	No target compound ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: SVOCs/SW846 8270D SIM
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when SVOCs are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	LCS/LCSD MS/MSD	RPD ≤ 25% when SVOCs are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks & Instrument Blank	No target compound ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: GRO/DRO/SW846 8015B
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when analytes are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	LCS/LCSD MS/MSD	RPD ≤ 25% when analytes are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks & Instrument Blank	No target compound ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil
Analytical Group or Method: PCBs/SW846 8082
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	RPD ≤ 50% when PCBs are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	LCS/LCSD MS/MSD	RPD ≤ 25% when PCBs are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Overall Accuracy/Bias (contamination)	Method Blanks & Instrument Blank*	No target compound ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

*Per the 10/1/15 email from EPA, Field and Equipment Blanks will not be analyzed for PCBs

Matrix: Aqueous
Analytical Group or Method: PCBs/SW846 680
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	RPD ≤ 30% when PCBs are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	LCS/LCSD MS/MSD	RPD ≤ 25% when PCBs are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Overall Accuracy/Bias (contamination)	Method Blanks & Instrument Blank*	No target compound ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

*Per the 10/1/15 email from EPA, Field and Equipment Blanks will not be analyzed for PCBs

Matrix: Soil and Aqueous
Analytical Group or Method: Metals/SW846 6010C
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when metals are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	Laboratory Duplicates MS/MSD	RPD ≤ 20% when metals are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	MS/MSD	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	Post-Digestion Spikes	Recovery + 25% of expected results
Analytical Accuracy/Bias (matrix interference)	Dilution Test	1:5 dilution must agree within + 10% of the original determination.
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks	No target analyte ≥ QL
Sensitivity	LOQ verification sample (spiked at LOQ)	Recovery within ±20% of LOQ
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil/Aqueous/Air
Analytical Group or Method: Mercury 7471A/7470A/NIOSH 6009
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30% Air: RPD ≤ 50%; when analytes are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	Laboratory Duplicates	RPD ≤ 20% when analytes are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Recovery ± 20% of expected results
Analytical Accuracy/Bias (matrix interference)	Matrix Spike	Recovery ± 25% of expected results
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks	No target analytes ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: Hexavalent Chromium/7196A
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when analytes are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	Laboratory Duplicates	RPD ≤ 20% when analytes are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Recovery ± 20% of expected results (solid); ± 15% (aqueous)
Analytical Accuracy/Bias (matrix interference)	Matrix Spike (Soluble)	Recovery ± 25% of expected results (solid); ± 15% (aqueous)
Analytical Accuracy/Bias (matrix interference)	Matrix Spike (Insoluble for solid matrix only)	Recovery ± 25% of expected results
Analytical Accuracy/Bias (matrix interference)	Post-Digestion Spike (solid matrix only)	Recovery ± 15% of expected results
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks	No target analytes ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: Cyanide/9012A
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when analytes are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	Laboratory Duplicates	RPD ≤ 20% when analytes are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Recovery $\pm$ 10% of expected results
Analytical Accuracy/Bias (matrix interference)	Matrix Spike	Recovery $\pm$ 10% of expected results
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks	No target analytes ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

Matrix: Soil and Aqueous
Analytical Group or Method: 9071B/1664
Concentration Level: Low

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	Soil: RPD ≤ 50% Aqueous: RPD ≤ 30%; when analytes are detected in both samples ≥ sample-specific QL
Analytical Precision (laboratory)	Laboratory Duplicates	RPD ≤ 34% when analytes are detected in both samples ≥ sample-specific QL
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	78-114% (HEM) 64-132% (SGT HEM)
Analytical Accuracy/Bias (matrix interference)	Matrix Spike	78-114% (HEM) 64-132% (SGT HEM)
Overall Accuracy/Bias (contamination)	Equipment Blanks, Field Blanks, Method Blanks	No target analytes ≥ QL
Sensitivity	Laboratory Fortified Blank at the QL	The laboratory's own in-house criteria
Completeness	See Worksheet #34	See Worksheet #34

QAPP Worksheet #13: Secondary Data Uses and Limitations
(UFP-QAPP Manual Section 2.7)
(EPA 2106-G-05 Chapter 3: QAPP Elements For Evaluating Existing Data)

A large amount of existing data is available in previous site investigation reports.

In general, the existing data has primarily been utilized to develop the conceptual site model and to identify potential sources and areas of interest for the project. It is anticipated that this data will continue to be used over the course of the investigations.

The Table provided below discusses the use of existing data.

Data type	Source	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
Site activities	Bethlehem Steel Plant Drawings 5000 Set (Plant Arrangement) 5100 Set (Plant Index) 5500 Set (Plant Sewer Lines) coke oven gas distribution drip leg locations	Identification of Potential Sources of Releases and Areas of Interest	Drawings are difficult to read and accurate locations may be difficult to determine
Site activities and Geologic data	Description of Current Conditions Report, (DCCR) Rust 1998	Identification of Potential Sources of Releases and Areas of Interest General site geology	Accuracy of many of the drawings is limited or not to scale Descriptions of geology is limited to general stratigraphy
Hydrologic and Groundwater data	Site-Wide Investigation Release Site Characterization Study, June 2002 (CH2M Hill 2002a)	Identification of Potential Sources of Releases and Areas of Interest Site geology and hydrogeology	Provides significant amount of geologic data considered useable. Groundwater data do not reflect current conditions
Hydrologic, geologic, and Groundwater data	Site-Wide Investigation: Report of Nature & Extent of Releases to Groundwater From the Special Study Areas, International Steel Group, ISG Sparrows Point, Inc. Facility, Sparrows Point, Maryland, January 2005 (URS 2005a), revised 2007	Preliminary indications of Groundwater Flow. Identification of potential sources of release for soil investigations.	Provides significant amount of geologic data considered useable. Groundwater data do not reflect current conditions

	CA725 Facility Investigation and Human Health Risk Evaluation (HHRE) Findings, ISG Sparrows Point, June 2005 (URS 2005b)		Data greater than ten years old and does not reflect current conditions
Soil data Sediment data Surface Water data	Screening Level Ecological Risk Assessment For On-Site Areas Final (April 2009, URS)	Data to use in conjunction with newly collected data for characterization of the site	Limited to a portion of the site
Soil data Sediment data Surface Water data	Supplemental Report, County Lands Parcel 1B Ponds (URS 2009b)	Data to use in conjunction with newly collected data for characterization of the site	Limited to a portion of the site
Ecological Risk	Final Baseline Ecological Risk Assessment for On-Site Areas (BERA) Report (URS, October 7, 2011)	Identification of Ecological Risk Endpoints	Limited to a portion of the site
System Data from existing Interim Measures	Progress Reports, continued monitoring data	Evaluation of current Interim Measures and Evaluation of remedial alternatives	No significant limitations are known.
Site history	Phase I Environmental Site Assessment (Phase I), (Weaver Boos Consultants, LLC, 2014)	Identification of Potential Sources of Releases and Areas of Interest.	Some site observations but primarily based on secondary sources.

QAPP Worksheet #14/16: Project Tasks & Schedule
(UFP-QAPP Manual Section 2.8.2)
(EPA 2106-G-05 Section 2.2.4)

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Utility Clearance	Consultant/EAG			Miss Utility Ticket	48 hours prior to intrusive investigations
Mobilization	Consultant/ Field Manager				
Field Investigations	Consultant/Field Manager			Field Notes Field Progress Meetings	Following completion of task or task phase. Report to EAG Project Manager Weekly.
Soil Sample Collection	Consultant			Field Notes	Following completion of task or task phase.
Groundwater Sample Collection	Consultant			Field Notes/Purge Logs	Following completion of task or task phase.
Soil Gas Sample Collection	Consultant			Field Notes	Following completion of task or task phase.
Monthly Reporting	Consultant			Monthly letter summarizing results to EAG/MDE for field work of longer duration	After the end of each month of field implementation
Sample Analysis	PACE	Following Sample Collection	10 days after receipt	Level II Data Package Level IV Data Package	10 days after sample receipt. 1 month after sample receipt
Level 2B Validation	EDQI	Following receipt of Level IV Data Package		Data Validation Report (DVR)	6 weeks following sample receipt
Investigation Report Preparation	Consultant	Following receipt of DVR	6 weeks after DVR receipt	Draft Phase II Site Investigation Report	6 weeks following DVR receipt
Bench Scale Treatability Testing	EAG	Upon Recovery of Sample Materials	4 to 6 weeks, up to 3 months (in which case EPA/MDE will be notified)	Phase II Pre-Design Investigation Summary Report	8 weeks after Bench Scale Testing

QAPP Worksheet #15: Project Action Limits and Laboratory-Specific Detection/Quantitation Limits
(UFP-QAPP Manual Section 2.6.2.3 and Figure 15)
(EPA 2106-G-05 Section 2.2.6)

Matrix: Soil Gas
Analytical Method: TO-15
Concentration level (if applicable): Low

Analyte	Project Action Limit (μg/m3)	PAL Reference	Project Quantitation Limit Goal (μg/m3)	Laboratory specific quantitation limit (μg/m3)	Laboratory specific detection-limit[1] (μg/m3)
1,1,1-Trichloroethane	2.2×10^{6}	MD Tier I SV	1.09	1.09	0.189
1,1,2,2-Tetrachloroethane	2.2×10^{2}	MD Tier I SV	1.37	1.37	0.251
1,1,2-Trichloroethane	8.8×10^{1}	MD Tier I SV	1.09	1.09	0.233
1,1-Dichloroethane	7.7×10^{3}	MD Tier I SV	0.809	0.809	0.0987
1,1-Dichloroethene	8.8×10^{4}	MD Tier I SV	0.793	0.793	0.0484
1,2-Dibromoethane	2.1×10^{1}	MD Tier I SV	1.54	1.54	0.195
1,2-Dichloroethane	4.8×10^{2}	MD Tier I SV	0.809	0.809	0.0617
1,2-Dichloroethene (trans)	2.7×10^{4}	MD Tier I SV	0.810	0.810	0.0685
1,2-Dichloropropane	1.3×10^{3}	MD Tier I SV	0.924	0.924	0.169
2-Butanone (MEK)	2.2×10^{6}	MD Tier I SV	0.589	0.589	0.072
4-Methyl-2-pentanone (MIBK)	1.4×10^{6}	MD Tier I SV	0.818	0.819	0.100
Acetone	1.4×10^{7}	MD Tier I SV	0.475	0.475	0.0749
Benzene	1.6×10^{3}	MD Tier I SV	0.639	0.639	0.11
Bromodichloromethane	3.4×10^{2}	MD Tier I SV	1.34	1.34	0.245
Bromoform	1.1×10^{4}	EPA RSL Industrial	2.07	2.07	0.273
Bromomethane	2.2×10^{3}	MD Tier I SV	0.769	0.769	0.0592
Carbon Disulfide	3.1×10^{5}	MD Tier I SV	0.621	0.621	0.0475

Analyte	Project Action Limit (μg/m3)	PAL Reference	Project Quantitation Limit Goal (μg/m3)	Laboratory specific quantitation limit (μg/m3)	Laboratory specific detection-limit[1] (μg/m3)
Carbon tetrachloride	2.1×10^{3}	MD Tier I SV	1.258	1.258	0.198
Chlorobenzene	2.2×10^{4}	MD Tier I SV	0.916	0.916	0.145
Chloroethane	4.4×10^{6}	MD Tier I SV	0.523	0.523	0.059
Chloroform	5.4×10^{2}	MD Tier I SV	0.965	0.965	0.074
Chloromethane	4.0×10^{4}	MD Tier I SV	0.409	0.409	0.0525
cis-1,2-Dichloroethene	2.7×10^{4}	MD Tier I SV	0.785	0.785	0.0685
cis-1,3-Dichloropropene	3.1×10^{3}	MD Tier I SV	0.899	0.899	0.0554
Dibromochloromethane	4.6×10^{2}	MD Tier I SV	1.68	1.68	0.147
Ethyl Benzene	5.0×10^{3}	MD Tier I SV	0.867	0.867	0.159
Isopropylbenzene	1.8×10^{5}	MD Tier I SV	2.45	2.45	0.123
Methyl Tert Butyl Ether	4.8×10^{4}	MD Tier I SV	0.72	0.72	0.0623
Methylene chloride	2.7×10^{5}	MD Tier I SV	0.687	0.687	0.215
Styrene	4.4×10^{5}	MD Tier I SV	0.850	0.850	0.0953
Tetrachloroethene	1.8×10^{4}	MD Tier I SV	1.36	1.36	0.117
Toluene	2.2×10^{6}	MD Tier I SV	0.753	0.753	0.0958
trans-1,2-dichloroethene	2.7×10^{4}	MD Tier I SV	0.810	0.810	0.0685
trans-1,3-Dichloropropene	3.1×10^{3}	MD Tier I SV	0.899	0.899	0.161
Trichloroethene	8.8×10^{2}	MD Tier I SV	1.07	1.07	0.12
Vinyl chloride	2.8×10^{3}	MD Tier I SV	0.507	0.507	0.0442
Xylenes (total)	4.4×10^{4}	MD Tier I SV	0.868	0.868	0.159
1,4-Dioxane	2.5×10^{2}	EPA RSL Industrial	1.799	1.799	0.271
1,2-Dibromo-3-chloropropane[2]	2.1×10^{0}	MD Tier I SV	Library Search	Library Search	N/A
1,2,3-Trichlorobenzene[2]	---	No EPA or MDE STD	Library Search	Library Search	N/A
1,2,4-Trichlorobenzene	8.8×10^{2}	MD Tier I SV	0.983	0.983	0.085
1,2-Dichlorobenzene	8.8×10^{4}	MD Tier I SV	1.202	1.202	0.11
1,4-Dichlorobenzene	1.2×10^{3}	MD Tier I SV	1.202	1.202	0.208

[1]Laboratory-specific MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method. MDLs may be subject to update

[2]A library search will be performed to tentatively identify this compound.

Matrix: Soil
Analytical Method: 8260B
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Acetone	670,000	EPA RSL Industrial Soil	0.01	0.01	0.00489
Benzene	5.1	EPA RSL Industrial Soil	0.005	0.005	0.00136
Bromodichloromethane	1.3	EPA RSL Industrial Soil	0.005	0.005	0.0013
Bromoform	86	EPA RSL Industrial Soil	0.005	0.005	0.00412
Bromomethane	30	EPA RSL Industrial Soil	0.005	0.005	0.00437
2-Butanone (Methyl Ethyl Ketone)	190000	EPA RSL Industrial Soil	0.01	0.01	0.00211
Carbon Disulfide	3500	EPA RSL Industrial Soil	0.005	0.005	0.00289
Carbon Tetrachloride	2.9	EPA RSL Industrial Soil	0.005	0.005	0.00445
Chlorobenzene	1300	EPA RSL Industrial Soil	0.005	0.005	0.00068
Chloroethane	57000	EPA RSL Industrial Soil	0.005	0.005	0.00186
Chloroform	1.4	EPA RSL Industrial Soil	0.005	0.005	0.00272
Chloromethane	460	EPA RSL Industrial Soil	0.005	0.005	0.00249
Dibromochloromethane	3.3	EPA RSL Industrial Soil	0.005	0.005	0.00154
1,2-dibromo-3-chloropropane	0.064	EPA RSL Industrial Soil	0.005	0.005	0.00195
1,2-Dibromoethane (Ethylene Dibromide)	0.16	EPA RSL Industrial Soil	0.005	0.005	0.00127
1,1-Dichloroethane	16	EPA RSL Industrial Soil	0.005	0.005	0.00263
1,2-Dichloroethane	2	EPA RSL Industrial Soil	0.005	0.005	0.00106
1,1-Dichloroethene	1000	EPA RSL Industrial Soil	0.005	0.005	0.00287
cis-1,2-Dichloroethene	2300	EPA RSL Industrial Soil	0.005	0.005	0.00182
trans-1,2-Dichloroethene	23000	EPA RSL Industrial Soil	0.005	0.005	0.00294
1,2-Dichloropropane	4.4	EPA RSL Industrial Soil	0.005	0.005	0.0012
1,3-Dichloropropene	8.2	EPA RSL Industrial Soil	0.005	0.005	0.00131

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Ethylbenzene	25	EPA RSL Industrial Soil	0.005	0.005	0.00101
Isopropylbenzene (Cumene)	9900	EPA RSL Industrial Soil	0.005	0.005	0.00173
4-Methyl-2-pentanone (Methyl Isobutyl	56000	EPA RSL Industrial Soil	0.01	0.01	0.0017
Methylene Chloride (Dichloromethane)	1000	EPA RSL Industrial Soil	0.005	0.005	0.00365
Methyl tert-butyl ether (MTBE)	210	EPA RSL Industrial Soil	0.005	0.005	0.00243
Styrene	35000	EPA RSL Industrial Soil	0.005	0.005	0.00113
Tetrachloroethene	100	EPA RSL Industrial Soil	0.005	0.005	0.00293
1,1,2,2-Tetrachloroethane	2.7	EPA RSL Industrial Soil	0.005	0.005	0.0014
Toluene	47000	EPA RSL Industrial Soil	0.005	0.005	0.00156
1,1,1-Trichloroethane	36000	EPA RSL Industrial Soil	0.005	0.005	0.00207
1,1,2-Trichloroethane	5	EPA RSL Industrial Soil	0.005	0.005	0.00113
Trichloroethene	6	EPA RSL Industrial Soil	0.005	0.005	0.00222
Vinyl Chloride	1.7	EPA RSL Industrial Soil	0.005	0.005	0.00289
Xylenes	2800	EPA RSL Industrial Soil	0.015	0.015	0.00284
Dichlorodifluoromethane	370	EPA RSL Industrial Soil	0.005	0.005	0.00361
Trichlorofluoromethane	3100	EPA RSL Industrial Soil	0.005	0.005	0.00306
1,1,2-Trichloro-1,2,2-trifluoroethane	170000	EPA RSL Industrial Soil	0.05	0.05	0.00364
Methyl Acetate	1200000	EPA RSL Industrial Soil	0.05	0.05	0.00214
Cyclohexane	27000	EPA RSL Industrial Soil	0.01	0.01	0.00343
2-Hexanone	1300	EPA RSL Industrial Soil	0.01	0.01	0.00143
1,2-Dichlorobenzene	9300	EPA RSL Industrial Soil	0.005	0.005	0.00061
1,3-Dichlorobenzene	---	No EPA RSL	0.005	0.005	0.00078
1,4-Dichlorobenzene	11	EPA RSL Industrial Soil	0.005	0.005	0.00085
1,2,3-Trichlorobenzene	930	EPA RSL Industrial Soil	0.005	0.005	0.00105
1,2,4-Trichlorobenzene	110	EPA RSL Industrial Soil	0.005	0.005	0.00106
1,4-Dioxane	24	EPA RSL Industrial Soil	0.100	0.100	0.0512

Matrix: Aqueous
Analytical Method: 8260B
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Acetone	14000	EPA RSL Tapwater	10	10	2.27
Benzene	5	EPA MCL Drinking Water	1	1	0.163
Bromodichloromethane	0.13	EPA RSL Tapwater	1	1	0.154
Bromoform	3.3	EPA RSL Tapwater	1	1	0.306
Bromomethane	7.5	EPA RSL Tapwater	1	1	0.58
2-Butanone (Methyl Ethyl Ketone)	5600	EPA RSL Tapwater	10	10	2.41
Carbon Disulfide	810	EPA RSL Tapwater	1	1	0.316
Carbon Tetrachloride	5	EPA MCL Drinking Water	1	1	0.216
Chlorobenzene	100	EPA MCL Drinking Water	1	1	0.13
Chloroethane	21000	EPA RSL Tapwater	1	1	0.692
Chloroform	0.22	EPA RSL Tapwater	1	1	0.186
Chloromethane	190	EPA RSL Tapwater	1	1	0.265
Dibromochloromethane	0.17	EPA RSL Tapwater	1	1	0.17
1,2-dibromo-3-chloropropane	0.2	EPA MCL Drinking Water	5	5	0.85
1,2-Dibromoethane (Ethylene Dibromide,	0.0075	EPA RSL Tapwater	1	1	0.191
1,1-Dichloroethane	2.7	EPA RSL Tapwater	1	1	0.186
1,2-Dichloroethane	5	EPA MCL Drinking Water	1	1	0.362
1,1-Dichloroethene	7	EPA MCL Drinking Water	1	1	0.259
cis-1,2-Dichloroethene	70	EPA MCL Drinking Water	1	1	0.232
trans-1,2-Dichloroethene	100	EPA MCL Drinking Water	1	1	0.215
1,2-Dichloropropane	5	EPA MCL Drinking Water	1	1	0.227
1,3-Dichloropropene	0.47	EPA RSL Tapwater	1	1	0.274

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Ethylbenzene	700	EPA MCL Drinking Water	1	1	0.232
Isopropylbenzene (Cumene)	450	EPA RSL Tapwater	1	1	0.135
4-Methyl-2-pentanone (Methyl Isobutyl	1200	EPA RSL Tapwater	10	10	0.568
Methylene Chloride (Dichloromethane)	5	EPA MCL Drinking Water	1	1	0.59
Methyl tert-butyl ether (MTBE)	14	EPA RSL Tapwater	1	1	0.174
Styrene	100	EPA MCL Drinking Water	1	1	0.155
Tetrachloroethene	5	EPA MCL Drinking Water	1	1	0.286
1,1,2,2-Tetrachloroethane	0.076	EPA RSL Tapwater	1	1	0.227
Toluene	1000	EPA MCL Drinking Water	1	1	0.126
1,1,1-Trichloroethane	200	EPA MCL Drinking Water	1	1	0.287
1,1,2-Trichloroethane	5	EPA MCL Drinking Water	1	1	0.325
Trichloroethene	5	EPA MCL Drinking Water	1	1	0.327
Vinyl Chloride	2	EPA MCL Drinking Water	1	1	0.205
Xylenes	10000	EPA MCL Drinking Water	3	3	0.547
Dichlorodifluoromethane	200	EPA RSL Tapwater	1	1	0.494
Trichlorofluoromethane	1100	EPA RSL Tapwater	1	1	0.345
1,1,2-Trichloro-1,2,2-trifluoroethane	55000	EPA RSL Tapwater	50	50	0.47
Methyl Acetate	20000	EPA RSL Tapwater	5	5	1.23
Cyclohexane	13000	EPA RSL Tapwater	10	10	0.134
2-Hexanone	38	EPA RSL Tapwater	10	10	0.58
1,2-Dichlorobenzene	600	EPA MCL Drinking Water	1	1	0.187
1,3-Dichlorobenzene	---		1	1	0.134
1,4-Dichlorobenzene	75	EPA MCL Drinking Water	1	1	0.242
1,2,3-Trichlorobenzene	7	EPA RSL Tapwater	2	2	0.377
1,2,4-Trichlorobenzene	70	EPA MCL Drinking Water	1	1	0.39

Matrix: Solid
Analytical Method: 8270D
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Acenaphthene	45000	EPA RSL Industrial Soil	0.333	0.0666	0.015
Acenaphthylene	45000	EPA RSL Industrial Soil	0.333	0.0666	0.0145
Anthracene	230000	EPA RSL Industrial Soil	0.333	0.0666	0.0156
Benz[a]anthracene	2.9	EPA RSL Industrial Soil	0.333	0.0666	0.013
Benzo[a]pyrene	0.29	EPA RSL Industrial Soil	0.333	0.0666	0.0098
Benzo[b]fluoranthene	2.9	EPA RSL Industrial Soil	0.333	0.0666	0.0125
Benzo[g,h,i]perylene	---	No EPA RSL	0.333	0.0666	0.0132
Benzo[k]fluoranthene	29	EPA RSL Industrial Soil	0.333	0.0666	0.013
bis(2-Chloroethyl)ether	1	EPA RSL Industrial Soil	0.333	0.0666	0.0158
bis(2-Ethylhexyl)phthalate	160	EPA RSL Industrial Soil	0.333	0.0666	0.0134
Carbazole	---	No EPA RSL	0.333	0.0666	0.0158
4-Chloroaniline	11	EPA RSL Industrial Soil	1.65	0.0666	0.0151
2-Chloronaphthalene	60000	EPA RSL Industrial Soil	0.333	0.0666	0.0136
2-Chlorophenol	5800	EPA RSL Industrial Soil	0.333	0.0666	0.0161
Chrysene	290	EPA RSL Industrial Soil	0.333	0.0666	0.0136
Dibenz[a,h]anthracene	0.29	EPA RSL Industrial Soil	0.333	0.0666	0.0116
3,3-Dichlorobenzidine	5.1	EPA RSL Industrial Soil	0.333	0.0666	0.0129
2,4-Dichlorophenol	2500	EPA RSL Industrial Soil	0.333	0.0666	0.0177
Diethylphthalate	660000	EPA RSL Industrial Soil	0.333	0.0666	0.0134
2,4-Dimethylphenol	16000	EPA RSL Industrial Soil	0.333	0.0666	0.0132
Di-n-butylphthalate	82000	EPA RSL Industrial Soil	0.333	0.0666	0.0157
2,4-Dinitrophenol	1600	EPA RSL Industrial Soil	0.833	0.1666	0.0343
2,4-Dinitrotoluene	7.4	EPA RSL Industrial Soil	0.333	0.0666	0.0153
2,6-Dinitrotoluene	1.5	EPA RSL Industrial Soil	0.333	0.0666	0.0169

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Fluoranthene	30000	EPA RSL Industrial Soil	0.333	0.0666	0.0158
Fluorene	30000	EPA RSL Industrial Soil	0.333	0.0666	0.0155
Hexachlorobenzene	0.96	EPA RSL Industrial Soil	0.333	0.0666	0.0155
Hexachlorobutadiene	5.3	EPA RSL Industrial Soil	0.333	0.0666	0.0161
Hexachlorocyclopentadiene	7.5	EPA RSL Industrial Soil	0.333	0.0666	0.0119
Hexachloroethane	8	EPA RSL Industrial Soil	0.333	0.0666	0.0148
Indeno[1,2,3-c,d]pyrene	2.9	EPA RSL Industrial Soil	0.333	0.0666	0.0124
Isophorone	2400	EPA RSL Industrial Soil	0.333	0.0666	0.0182
2-Methylnaphthalene	3000	EPA RSL Industrial Soil	0.333	0.0666	0.0138
2-Methylphenol	41000	EPA RSL Industrial Soil	0.333	0.0666	0.013
3-Methylphenol	41000	EPA RSL Industrial Soil	0.333	0.1333	0.0164
4-Methylphenol	82000	EPA RSL Industrial Soil	0.333	0.1333	0.0164
Naphthalene	17	EPA RSL Industrial Soil	0.333	0.0666	0.0143
Nitrobenzene	22	EPA RSL Industrial Soil	0.333	0.0666	0.0166
N-Nitrosodiphenylamine	470	EPA RSL Industrial Soil	0.333	0.0666	0.0132
N-Nitroso-di-n-propylamine	0.33	EPA RSL Industrial Soil	0.333	0.0666	0.0158
Bis(2-Chloroisopropyl)ether	22	EPA RSL Industrial Soil	0.333	0.0666	0.164
Pentachlorophenol	4	EPA RSL Industrial Soil	0.833	0.1666	0.0312
Phenanthrene	---	No EPA RSL	0.333	0.0666	0.0155
Phenol	250000	EPA RSL Industrial Soil	0.333	0.0666	0.0159
Pyrene	23000	EPA RSL Industrial Soil	0.333	0.0666	0.0178
2,4,5-Trichlorophenol	82000	EPA RSL Industrial Soil	0.833	0.1666	0.0147
2,4,6-Trichlorophenol	210	EPA RSL Industrial Soil	0.333	0.0666	0.0164
Acetophenone	120000	EPA RSL Industrial Soil	0.333	0.0666	0.0161
Benzaldehyde	120000	EPA RSL Industrial Soil	0.333	0.0666	0.0146
1,1'-Biphenyl	200	EPA RSL Industrial Soil	0.333	0.0666	0.0138
Bis(2-Chloroethoxy) methane	2500	EPA RSL Industrial Soil	0.333	0.0666	0.0148
Caprolactam	400000	EPA RSL Industrial Soil	0.833	0.1666	0.0186

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
3,3'-Dichlorobenzidine	5.1	EPA RSL Industrial Soil	0.333	0.0666	0.0129
Di-n-octylphthalate	8200	EPA RSL Industrial Soil	0.333	0.0666	0.0181
2-Nitroaniline	8000	EPA RSL Industrial Soil	0.833	0.1666	0.0146
4-Nitroaniline	110	EPA RSL Industrial Soil	0.833	0.1666	0.0235
1,2,4,5-tetrachlorobenzene	350	EPA RSL Industrial Soil	0.333	0.0666	0.0149
2,3,4,6-Tetrachlorophenol	25000	EPA RSL Industrial Soil	0.333	0.0666	0.0142

Matrix: Aqueous
Analytical Method: 8270D
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Acenaphthene	530	EPA RSL Tapwater	1.0	1.0	0.234
Acenaphthylene	530	EPA RSL Tapwater	1.0	1.0	0.246
Anthracene	1800	EPA RSL Tapwater	1.0	1.0	0.126
Benz[a]anthracene	0.012	EPA RSL Tapwater	1.0	1.0	0.251
Benzo[a]pyrene	0.2	EPA MCL Drinking Water	1.0	1.0	0.111
Benzo[b]fluoranthene	0.034	EPA RSL Tapwater	1.0	1.0	0.182
Benzo[g,h,i]perylene	---	No EPA RSL	1.0	1.0	0.156
Benzo[k]fluoranthene	0.34	EPA RSL Tapwater	1.0	1.0	0.107
bis(2-Chloroethyl)ether	0.014	EPA RSL Tapwater	1.0	1.0	0.329
bis(2-Ethylhexyl)phthalate	6	EPA MCL Drinking Water	1.0	1.0	0.199
Carbazole	---	No EPA RSL	1.0	1.0	0.134

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
4-Chloroaniline	0.36	EPA RSL Tapwater	1.0	1.0	0.333
2-Chloronaphthalene	750	EPA RSL Tapwater	1.0	1.0	0.254
2-Chlorophenol	91	EPA RSL Tapwater	1.0	1.0	0.285
Chrysene	3.4	EPA RSL Tapwater	1.0	1.0	0.268
Dibenz[a,h]anthracene	0.0034	EPA RSL Tapwater	1.0	1.0	0.178
3,3-Dichlorobenzidine	0.12	EPA RSL Tapwater	20	20	0.587
2,4-Dichlorophenol	46	EPA RSL Tapwater	1.0	1.0	0.318
Diethylphthalate	15000	EPA RSL Tapwater	1.0	1.0	0.197
2,4-Dimethylphenol	360	EPA RSL Tapwater	1.0	1.0	0.461
Di-n-butylphthalate	900	EPA RSL Tapwater	1.0	1.0	0.106
2,4-Dinitrophenol	39	EPA RSL Tapwater	2.5	2.5	0.443
2,4-Dinitrotoluene	0.24	EPA RSL Tapwater	1.0	1.0	0.688
2,6-Dinitrotoluene	0.048	EPA RSL Tapwater	1.0	1.0	0.229
Fluoranthene	800	EPA RSL Tapwater	1.0	1.0	0.104
Fluorene	290	EPA MCL Drinking Water	1.0	1.0	0.235
Hexachlorobenzene	1	EPA MCL Drinking Water	1.0	1.0	0.119
Hexachlorobutadiene	0.14	EPA RSL Tapwater	1.0	1.0	0.259
Hexachlorocyclopentadiene	50	EPA MCL Drinking Water	1.0	1.0	0.604
Hexachloroethane	0.33	EPA RSL Tapwater	1.0	1.0	0.264
Indeno[1,2,3-c,d]pyrene	0.034	EPA RSL Tapwater	1.0	1.0	0.135
Isophorone	78	EPA RSL Tapwater	1.0	1.0	0.261
2-Methylnaphthalene	36	EPA RSL Tapwater	1.0	1.0	0.276
2-Methylphenol	930	EPA RSL Tapwater	1.0	1.0	0.279
3-Methylphenol	930	EPA RSL Tapwater	2.0	2.0	0.469
4-Methylphenol	1900	EPA RSL Tapwater	2.0	2.0	0.469
Naphthalene	0.17	EPA RSL Tapwater	1.0	1.0	0.309
Nitrobenzene	0.14	EPA RSL Tapwater	1.0	1.0	0.253
N-Nitrosodiphenylamine	12	EPA RSL Tapwater	1.0	1.0	0.389

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
N-Nitroso-di-n-propylamine	0.011	EPA RSL Tapwater	1.0	1.0	0.287
Bis(2-Chloroisopropyl)ether	0.36	EPA RSL Tapwater	1.0	1.0	0.267
Pentachlorophenol	1	EPA MCL Drinking Water	2.5	2.5	0.636
Phenanthrene	---	No EPA RSL	1.0	1.0	0.148
Phenol	5800	EPA RSL Tapwater	1.0	1.0	0.186
Pyrene	120	EPA RSL Tapwater	1.0	1.0	0.256
2,4,5-Trichlorophenol	1200	EPA RSL Tapwater	2.5	2.5	0.616
2,4,6-Trichlorophenol	4	EPA RSL Tapwater	1.0	1.0	0.593
Acetophenone	1900	EPA RSL Tapwater	1.0	1.0	0.288
Benzaldehyde	1900	EPA RSL Tapwater	1.0	1.0	0.700
1,1'-Biphenyl	0.83	EPA RSL Tapwater	1.0	1.0	0.286
Bis(2-Chloroethoxy)methane	59	EPA RSL Tapwater	1.0	1.0	0.259
Caprolactum	9900	EPA RSL Tapwater	2.5	2.5	0.143
3,3'-Dichlorobenzidine	0.12	EPA RSL Tapwater	1.0	1.0	0.587
Di-n-octylphthalate	200	EPA RSL Tapwater	1.0	1.0	0.217
2-Nitroaniline	190	EPA RSL Tapwater	2.5	2.5	0.583
4-Nitroaniline	3.8	EPA RSL Tapwater	2.5	2.5	0.319
1,2,4,5-Tetrachlorobenzene	1.7	EPA RSL Tapwater	1.0	1.0	0.270
2,3,4,6-Tetrachlorophenol	240	EPA RSL Tapwater	1.0	1.0	0.521

Matrix: Solid
Analytical Method: 8270D SIM
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Acenaphthene	45000	EPA RSL Industrial Soil	0.0067	0.0067	0.00059
Acenaphthylene	45000	EPA RSL Industrial Soil	0.0067	0.0067	0.00057
Anthracene	230000	EPA RSL Industrial Soil	0.0067	0.0067	0.00065
Benz[a]anthracene	2.9	EPA RSL Industrial Soil	0.0067	0.0067	0.00171
Benzo[a]pyrene	0.29	EPA RSL Industrial Soil	0.0067	0.0067	0.00064
Benzo[b]fluoranthene	2.9	EPA RSL Industrial Soil	0.0067	0.0067	0.00059
Benzo[g,h,i]perylene	---	No EPA RSL	0.0067	0.0067	0.00103
Benzo[k]fluoranthene	29	EPA RSL Industrial Soil	0.0067	0.0067	0.00063
Chrysene	290	EPA RSL Industrial Soil	0.0067	0.0067	0.00044
Dibenz[a,h]anthracene	0.29	EPA RSL Industrial Soil	0.0067	0.0067	0.00088
Fluoranthene	30000	EPA RSL Industrial Soil	0.0067	0.0067	0.00044
Fluorene	30000	EPA RSL Industrial Soil	0.0067	0.0067	0.00058
Indeno[1,2,3-c,d]pyrene	2.9	EPA RSL Industrial Soil	0.0067	0.0067	0.00079
2-Methylnaphthalene	3000	EPA RSL Industrial Soil	0.0067	0.0067	0.00086
Naphthalene	17	EPA RSL Industrial Soil	0.0067	0.0067	0.00094
Phenanthrene	---	No EPA RSL	0.0067	0.0067	0.00067
Pyrene	23000	EPA RSL Industrial Soil	0.0067	0.0067	0.00054

Matrix: Aqueous
Analytical Method: 8270D SIM
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Acenaphthene	530	EPA RSL Tapwater	0.1	0.1	0.0157
Acenaphthylene	530	EPA RSL Tapwater	0.1	0.1	0.0142
Anthracene	1800	EPA RSL Tapwater	0.1	0.1	0.0125
Benz[a]anthracene	0.012	EPA RSL Tapwater	0.1	0.1	0.0144
Benzo[a]pyrene	0.2	EPA MCL Drinking Water	0.1	0.1	0.0071
Benzo[b]fluoranthene	0.034	EPA RSL Tapwater	0.1	0.1	0.0157
Benzo[g,h,i]perylene	---	No EPA RSL	0.1	0.1	0.0188
Benzo[k]fluoranthene	0.34	EPA RSL Tapwater	0.1	0.1	0.0113
Chrysene	3.4	EPA RSL Tapwater	0.1	0.1	0.0075
Dibenz[a,h]anthracene	0.0034	EPA RSL Tapwater	0.1	0.1	0.028
Fluoranthene	800	EPA RSL Tapwater	0.1	0.1	0.0105
Fluorene	290	EPA RSL Tapwater	0.1	0.1	0.016
Indeno[1,2,3-c,d]pyrene	0.034	EPA RSL Tapwater	0.1	0.1	0.0274
2-Methylnaphthalene	36	EPA RSL Tapwater	0.1	0.1	0.0206
Naphthalene	0.17	EPA RSL Tapwater	0.1	0.1	0.0177
Phenanthrene	---	No EPA RSL	0.1	0.1	0.0154
Pyrene	120	EPA RSL Tapwater	0.1	0.1	0.0125
1,4-Dioxane	0.46	EPA RSL Tapwater	0.1	0.1	0.1

Matrix: Soil
Analytical Method: 8015B
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Gasoline Range Organics (GRO)	620	MDE Non-Residential Soil Standard	10	10	5.4
Diesel Range Organics (DRO)	620	MDE Non-Residential Soil Standard	6.67	6.67	3.53

Matrix: Aqueous
Analytical Method: 8015B
Concentration level (if applicable): Low

Analyte	Project Action Limit (ug/L)	PAL Reference	Project Quantitation Limit Goal (ug/L)	Laboratory specific quantitation limit (ug/L)	Laboratory specific detection-limit[1] (ug/L)
Gasoline Range Organics (GRO)	47	MDE Groundwater Standard	200	200	74.0
Diesel Range Organics (DRO)	47	MDE Groundwater Standard	100	100	25.5

Matrix: Soil
Analytical Method: 8082
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
PCB(total)	0.97	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1016	27	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1221	0.72	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1232	0.72	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1242	0.97	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1248	0.94	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1254	0.97	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1260	0.99	EPA RSL Industrial Soil	0.0500	0.0500	0.0192
Aroclor 1262	---	No EPA RSL	0.0500	0.0500	0.0192
Aroclor 1268	---	No EPA RSL	0.0500	0.0500	0.0192

Matrix: Aqueous
Analytical Method: 680
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Monochlorobiphenyl	0.044	EPA RSL Tapwater	0.005	0.005	0.00130
Dichlorobiphenyl	0.044	EPA RSL Tapwater	0.005	0.005	0.00223
Trichlorobiphenyl	0.044	EPA RSL Tapwater	0.005	0.005	0.00184
Tetrachlorobiphenyl	0.0004	EPA RSL Tapwater	0.01	0.01	0.00383
Pentachlorobiphenyl	0.0000012	EPA RSL Tapwater	0.01	0.01	0.00360
Hexachlorobiphenyl	0.000004	EPA RSL Tapwater	0.01	0.01	0.00374
Heptachlorobiphenyl	0.004	EPA RSL Tapwater	0.015	0.015	0.00619
Octachlorobiphenyl	0.044	EPA RSL Tapwater	0.015	0.015	0.00536
Nonachlorobiphenyl	0.044	EPA RSL Tapwater	0.025	0.025	0.00535
Decachlorobiphenyl	0.044	EPA RSL Tapwater	0.025	0.025	0.00535
PCBs (total)	0.5	EPA MCL Drinking Water	0.025	0.025	0.00535

Matrix: Soil
Analytical Method: 6010C
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Aluminum	1100000	EPA RSL Industrial Soil	10	10	1.94
Antimony	470	EPA RSL Industrial Soil	0.6	0.6	0.27
Arsenic	3	EPA RSL Industrial Soil	0.5	0.5	0.428
Barium	220000	EPA RSL Industrial Soil	2	2	0.155
Beryllium	2300	EPA RSL Industrial Soil	0.2	0.2	0.0325
Cadmium	980	EPA RSL Industrial Soil	0.3	0.3	0.0759
Chromium (total)	---	No EPA RSL	0.5	0.5	0.0876
Copper	47000	EPA RSL Industrial Soil	1	1	0.155
Iron	820000	EPA RSL Industrial Soil	10	10	1.03
Lead	800	EPA RSL Industrial Soil	0.5	0.5	0.483
Manganese	26000	EPA RSL Industrial Soil	1.0	1.0	0.133
Nickel	22000	EPA RSL Industrial Soil	2	2	0.253
Selenium	5800	EPA RSL Industrial Soil	0.8	0.8	0.595
Silver	5800	EPA RSL Industrial Soil	0.6	0.6	0.0631
Thallium	12	EPA RSL Industrial Soil	2	2	0.524
Vanadium	5800	EPA RSL Industrial Soil	1.0	1.0	0.061
Zinc	350000	EPA RSL Industrial Soil	1	1	0.437
Cobalt	350	EPA RSL Industrial Soil	1	1	0.0737

Matrix: Aqueous
Analytical Method: 6010C
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Aluminum	20000	EPA RSL Tapwater	50	50	8.0
Antimony	6	EPA MCL Drinking Water	6	6	2.83
Arsenic	10	EPA MCL Drinking Water	5	5	4.46
Barium	2000	EPA MCL Drinking Water	10	10	0.795
Beryllium	4	EPA MCL Drinking Water	1	1	0.453
Cadmium	5	EPA MCL Drinking Water	3	3	0.551
Chromium (total)	100	EPA MCL Drinking Water	5	5	0.728
Copper	1300	EPA MCL Drinking Water	5	5	2
Iron	14000	EPA RSL Tapwater	70	70	8.92
Lead	15	EPA MCL Drinking Water	5	5	3.57
Manganese	430	EPA RSL Tapwater	5	5	0.493
Nickel	390	EPA RSL Tapwater	10	10	1.7
Selenium	50	EPA MCL Drinking Water	8	8	4.6
Silver	94	EPA RSL Tapwater	6	6	0.821
Thallium	2	EPA MCL Drinking Water	10	10	2.89
Vanadium	86	EPA RSL Tapwater	5	5	0.669
Zinc	6000	EPA RSL Tapwater	10	10	2.7
Cobalt	6	EPA RSL Tapwater	5	5	0.554

Matrix: Solid
Analytical Method: 7471B
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Mercury (total)	350	EPA Industrial Soil (Mercury Salts)	0.1	0.1	0.00241

Matrix: Aqueous
Analytical Method: 7470A
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Mercury (inorganic/Mercuric Dichloride)	2	EPA MCL Drinking Water	0.2	0.2	0.0217

Matrix: Air
Analytical Method: NIOSH 6009
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/m^3)	PAL Reference	Project Quantitation Limit Goal (µg/m^3)	Laboratory specific quantitation limit (µg/m^3)	Laboratory specific detection-limit[1] (µg/m^3)
Mercury	1.3	EPA RSL Industrial Air	12.0	12.0	1.0

Matrix: Soil
Analytical Method: 7196A
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Chromium VI	6.3	EPA RSL Industrial Soil	1	1	0.138

Matrix: Aqueous
Analytical Method: 7196A
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Chromium VI	0.035	EPA RSL Tapwater	10	10	3.14

Matrix: Solid
Analytical Method: 9012A
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Cyanide	150	EPA Industrial Soil	1	1	0.058

Matrix: Aqueous

Analytical Method: 9012A
Concentration level (if applicable): Low

Analyte	Project Action Limit (µg/L)	PAL Reference	Project Quantitation Limit Goal (µg/L)	Laboratory specific quantitation limit (µg/L)	Laboratory specific detection-limit[1] (µg/L)
Cyanide	200	EPA MCL Drinking Water	10	10	2.21

Matrix: Aqueous
Analytical Method: EPA 1664A
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/L)	PAL Reference	Project Quantitation Limit Goal (mg/L)	Laboratory specific quantitation limit (mg/L)	Laboratory specific detection-limit[1] (mg/L)
Oil and Grease	---	No EPA or MDE STD	5	5	0.902

Matrix: Solid
Analytical Method: EPA 9071B
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (mg/Kg)	Laboratory specific quantitation limit (mg/Kg)	Laboratory specific detection-limit[1] (mg/Kg)
Oil and Grease	---	No EPA or MDE STD	100	100	15.3

Matrix: Solid
Analytical Method: EPA 8290/8290A/SW3540
Concentration level (if applicable): Low

Analyte	Project Action Limit (mg/Kg)	PAL Reference	Project Quantitation Limit Goal (ng/Kg)	Laboratory specific quantitation limit (ng/Kg)	Laboratory specific detection-limit[1] (ng/Kg)
2,3,7,8-TCDF	---	No EPA RSL	1.0	1.0	0.278
2,3,7,8-TCDD	2.2e-5	EPA RSL Industrial Soil	1.0	1.0	0.202
1,2,3,7,8-PeCDF	---	No EPA RSL	5.0	5.0	0.601
2,3,4,7,8-PeCDF	---	No EPA RSL	5.0	5.0	0.583
1,2,3,7,8-PeCDD	---	No EPA RSL	5.0	5.0	0.584
1,2,3,4,7,8-HxCDF	---	No EPA RSL	5.0	5.0	0.624
1,2,3,6,7,8-HxCDF	---	No EPA RSL	5.0	5.0	0.536
2,3,4,6,7,8-HxCDF	---	No EPA RSL	5.0	5.0	0.655
1,2,3,7,8,9-HxCDF	---	No EPA RSL	5.0	5.0	0.761
1,2,3,4,7,8-HxCDD	---	No EPA RSL	5.0	5.0	0.776
1,2,3,6,7,8-HxCDD	---	No EPA RSL	5.0	5.0	0.663

1,2,3,7,8,9-HxCDD	---	No EPA RSL	5.0	5.0	0.723
1,2,3,4,6,7,8-HpCDF	---	No EPA RSL	5.0	5.0	0.792
1,2,3,4,7,8,9-HpCDF	---	No EPA RSL	5.0	5.0	0.726
1,2,3,4,6,7,8-HpCDD	---	No EPA RSL	5.0	5.0	0.692
OCDF	---	No EPA RSL	10.0	10.0	1.95
OCDD	---	No EPA RSL	10.0	10.0	1.40
Total TCDD [3]	2.2e-5	EPA RSL Industrial Soil	1.0	1.0	0.202
Total HxCDD	4.7e-4	EPA RSL Industrial Soil	15.0	15.0	2.16

[3] WHO 2005 TEF approach will be used to equate the applicable dioxin/furan congener results to 2,3,7,8-TCDD equivalencies for comparison to the PAL.

QAPP Worksheet #17: Sampling Design and Rationale
(UFP-QAPP Manual Section 3.1.1)
(EPA 2106-G-05 Section 2.3.1)

This document covers data that will be collected from 2015 through the completion of the site wide investigation and remediation. The sampling design is dependent on the objectives of the proposed investigation or monitoring task. Specific sampling locations for each task of the investigation will be presented in the task work plans. These proposed locations will be translated to the field through the use of a handheld GPS unit in accordance with SOP#20 – Field Location of Sample Points.

Media to be sampled and the relevant SOPs will include:

1. surface and subsurface soil; (SOP 008 and SOP 009)
2. groundwater (SOP 006);
3. surface water (SOP 004);
4. sediment (SOP 003);
5. soil gas (SOP 002); and
6. indoor air (SOP 001).

- **Phase II Investigations**

Phase II Investigations are planned for the entire site, as necessary to address data gaps, and specifically for the Carve-Out Areas where there has been little or no previous sampling conducted. Sampling locations have been or will be selected to:

1. determine presence or absence of contamination; and
2. characterize impacted areas to support risk assessment.

Several areas in and around the buildings and facilities may have been historical sources of environmental contamination. These areas will be identified as targets for sampling through a careful review of historical documents. When a sampling target is identified, one or more sample locations will be placed at or next to its location using GIS software (ArcMap Version 10.2.2).

The first sampling targets to be identified were Recognized Environmental Conditions (RECs) located within the Site boundaries, as shown on the REC Location Map provided in the Phase I Environmental Site Assessment (ESA) prepared by Weaver Boos Consultants dated May 19, 2014. Additional Findings (non-RECs) from the Phase I ESA which were identified as Potential Environmental Concerns are also reviewed and targeted as applicable.

Following the identification and evaluation of all RECs at the Site, Solid Waste Management Units (SWMUs) and Areas of Concern (AOCs) are identified from the Description of Current Conditions (DCC) report (Rust, 1998).

In some cases, there is additional information that can help confirm the location (e.g., if the REC or SWMU is visible on the aerial photograph or there is physical evidence remaining in the field).

Following the identification of all SWMUs and AOCs, four (4) sets of historical site drawings are reviewed to identify additional sampling targets. These site drawings included the 5000 Set (Plant Arrangement), the 5100 Set (Plant Index), the 5500 Set (Plant Sewer Lines), and a set of drawings indicating coke oven gas distribution drip leg locations. Sampling target locations were identified if the historical site drawings depicted industrial activities or a specific feature at a location that may have been a source of environmental contamination that impacted the Site. Based on this criterion, sampling targets identified at the Site may include: motor rooms, scale pits or handling areas, pump houses, fuel storage, other storage tanks, lube shops or rooms, soaking or other pits, sumps, trenches, process shops, furnaces, drip legs, settle basins, transformer storage areas, machine rooms, shears, and coal bins.

The work plans for the Phase II investigation of each parcel will include a table listing the available drawings for that parcel, and providing the original date of each drawing and the date that each drawing was last updated. The available historical site drawings are generally hand drawn from survey data. Building locations are likely to be reliable although some features within the buildings may have changed with maintenance and modifications over the years that may not be reflected in the drawing set. Some data, such as drip leg locations were hand-notations onto the base without survey. Therefore, these notations likely reflect the general locations of these features but specific locations may not be accurate.

These historical drawings were scanned and geo-rectified to enter into the GIS database. This also introduces some uncertainty into the location of targets.

Most of the identified targets are large enough (buildings, scale pits, etc.) that the location uncertainty is small relative to the size of the target itself. In some cases, the location of the target can also be confirmed on aerial photographs or by physical evidence on the ground.

Surface and Sub-surface Soil

Surface soil will be characterized by samples collected from the top 1 ft. Subsurface soil at depths of 1 ft to 10 ft below ground surface (bgs) will be characterized by sampling at intervals of 4-5 ft bgs and 9-10 ft bgs.

A biased approach has been utilized in the sampling design for the soil investigations to ensure that areas with the highest concentrations would be expected are sampled to minimize the potential for falsely rejecting the assumption that soil concentrations on individual parcels are present above the

Project Action Levels (PALs). Soil sample locations will be selected for each parcel to investigate each of the targets identified as described above. The number of proposed borings within a specific target is directly related to the size and the degree of uncertainty in the location of the target. If the location of a small target (<1 ac) can be confirmed on aerial photographs or by physical evidence in the field, then at least 2 borings per small target will be collected. Additional borings in the location of a small target maybe necessary based upon field conditions and REC characteristics. If the target is indicated as a larger area on the REC Location Map or historical drawings, 3 locations or more for identified large RECs will be included. The exact number of samples per large REC will be determined by REC specific factors and field conditions. Once all sampling targets are identified, additional sample locations (identified as site-wide sample locations) will be added to fill in areas and provide sufficient coverage (large spatial gaps between proposed samples) within the Carve-Out Areas. These borings will be spaced approximately evenly in areas between targets. In addition, if the known development plan includes paving or capping of an area, the distance between sample locations may be increased. In general, the sampling program for soil will be designed to ensure that the overall total number of samples (including both the targeted and site-wide sampling locations) within a parcel will meet the minimum density shown in the table below:

Parcel Size (acres)	Number of Samples	
	Engineered Barrier Proposed	No Engineered Barrier
<1	2	3
1 to 15	0.5 per acre with no less than 2	1 per acre with no less than 3
16 to 40	1 per 3 acres with no less than 7	1 per 1.5 acres with no less than 15
41 to 70	1 per 4 acres with no less than 13	1 per 2 acres with no less than 27
71 to 100	1 per 5 acres with no less than 17	1 per 2.5 acres with no less than 35
>100	1 per 6 acres with no less than 20	1 per 3 acres with no less than 40

Groundwater

Groundwater quality will be characterized through the sampling of existing wells, where possible, and the installation and sampling of new temporary or permanent wells in the shallow and intermediate flow zones. A biased approach has been developed to locate groundwater monitoring wells within the

Site area with the goal of intersecting the estimated plume areas from potential sources of groundwater contamination. Estimated plume areas for potential sources were delineated hydrogeologically downgradient of its location using the historical groundwater contour map of the Site adapted from Figure 3-1: Shallow Hydrogeologic Zone Groundwater Flow Contours June 2004 from the Site Wide Investigation Report of Nature & Extent of Releases to Groundwater from the Special Study Areas prepared by URS, dated January 2005. . Using these contours, each estimated plume area was initially delineated as an isosceles triangle having a 3:1 height-to-width ratio. The top vertex of the triangle coincides with location of the potential source, and the width of the triangle increases farther from the source location. This concept of a plume is based on an elongated plume model described in *An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species* (Domenico, P.A. 1992).

Proposed groundwater monitoring wells will be located around the perimeter of the Site ('perimeter wells') in intervals designed to intersect the calculated plume areas and detect potentially present contamination downgradient of potential sources. In addition to the perimeter wells, source specific groundwater monitoring points will also be located in the interior of the Site ('near-field wells') chosen to further target areas with a high concentration of potential sources. All near field groundwater monitoring wells will be installed to monitor groundwater in the shallow, unconfined zone. The perimeter well network will include shallow zone wells, with paired intermediate zone wells at a subset of the well location.

Sub-slab Soil Gas

Sub-slab soil gas samples will be collected in areas where existing buildings floor slabs are proposed to remain for re-use. Historic drawings are reviewed and existing buildings are visually inspected to identify target locations where volatile constituents would be expected. The sampling design for soil gas samples will ensure that sub-slab soil gas samples are collected at a frequency of at least 1 sample per 20,000 sf of building area, with a minimum of 3 samples for buildings < 20,000 sf. At least 2 sub-slab soil gas samples will be collected for each identified REC, and additional sample locations may be necessary depending on REC characteristics.

Soil Gas

Soil gas samples will be collected in areas where existing buildings are proposed to remain for re-use and there is no existing floor slab. Historic drawings are reviewed and existing buildings are visually inspected to identify target locations where volatile constituents would be expected. Soil gas samples may also be collected in areas where new buildings are proposed and soil gas, soil or groundwater sampling indicates a potential for unacceptable vapor intrusion. The sampling design for soil gas samples will ensure that soil gas samples are collected at a frequency of at least 1 sample per 20,000 sf of building area, with a minimum of 3 samples for building areas < 20,000 sf. At least 2 soil gas samples will be collected for each identified REC, and additional sample locations may be necessary depending on REC characteristics.

Indoor Air

Indoor air will be investigated in the event that soil gas, soil or groundwater sampling indicates a potential for unacceptable vapor intrusion. If required, the sampling design will ensure that indoor air samples are collected at a frequency of at least 1 sample per 20,000 sf of building area, with a minimum of 3 samples for building areas < 20,000 sf, and will be paired with the soil gas locations. Variations in building interiors may also necessitate additional indoor air sample locations.

Sediment

Sediment sampling will be designed to investigate significant on-site water bodies that are potential environmental concerns. Initial samples will be places at the upstream, center and downstream reaches of the water body on the site. If initial results indicate that risk assessment is required, adequate additional samples to characterize ecological habitat and/or potential human health exposure will be collected.

Surface Water

Initial sampling of on-site surface water will include at least three samples within each on-site water body that are potential environmental concerns. If initial results indicate that risk assessment will be required, adequate additional samples to characterize ecological habitat and/or potential human health exposure will be collected. Independent data points may include spatially distinct locations as well as temporally distinct samples from the same location.

- **Pre-Design Investigations**

Based upon a 1994 RCRA Facility Assessment and a 1998 Description of Current Conditions Report, EPA and MDE determined that further investigation and/or action was needed at 81 solid waste management units (SWMUs) and 28 Areas of Concern at the Property. The BSC Consent Decree organized these SWMUs and Areas of Concern into five (5) designated "Special Study Areas (SSAs)" to be focused upon during RCRA Corrective Action activities: the Tin Mill Canal/Finishing Mills, Greys Landfill, Humphreys Impoundment, Coke Point Landfill, and the Coke Oven Areas. Sampling locations have been or will be selected to:

1. delineate the nature and extent of identified contamination requiring remedial action;
2. gather data to support the evaluation and design of remedial alternatives; and
3. assess the methods and requirements for the proper handling and recycling/disposal of any removed materials.

The sampling design for Pre-Design Investigations is more focused than that for the Phase II Investigations since available groundwater data and historical information for the Special Study Areas provides more supporting information than is available for the Carve-out Areas. For example, locations for sampling of previously identified impacted areas may be designed to delineate around existing

sample locations and analysis may be limited to the COPIs identified for that area. Thus, the sampling design for the Pre-Design Investigations will be dictated by the needs to fill specific data gaps needed to support remedy selection and/or design.

- **Performance Monitoring**

Sampling locations have been or will be selected to:

1. monitor the progress of interim measures (IMs) and remedial actions; and
2. demonstrate the attainment of remedial action objectives.

QAPP Worksheet #18: Sampling Locations and Methods
(UFP-QAPP Manual Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Section 2.3.1 and 2.3.2)

This document covers data that will be collected from 2015 through the completion of the site wide investigation and remediation. Work plans have been or are to be developed for specific areas of the site and specific types of investigations. Future sampling locations will be in accordance with the relevant work plans and will be labeled in accordance with the identification requirements of the Data Management Plan. The sample types to be collected and analyzed include soil, groundwater, surface water, soil gas, and sediments. Each of these media requires specific methods for collection and handling, as outlined in the relevant SOPs for each sample type.

Media to be sampled and the relevant SOPs will include:

1. surface and subsurface soil; (SOP 008 and SOP 009)
2. groundwater (SOP 006);
3. surface water (SOP 004);
4. sediment (SOP 003);
5. soil gas (SOP 002); and
6. indoor air (SOP 001).

A general description of these listed sample types is presented here:

Soils: Soil samples may include material from multiple depth intervals, which are identified from project-specific planning documents. Sample locations are specified in the project work plan. Coordinates for the sample locations are generated from the GIS database and downloaded to a handheld GPS. The locations are acquired in the field via the use of handheld GPS in accordance with SOP 020 and staked for sample collection. The handheld GPS will provide for acquiring proposed sample locations in the field to an accuracy of within 3 meters (typically 1 meter) of the locations specified in the work plan.. Surface and shallow soil samples may be collected using a shovel, hand auger or direct push samplers. Deeper soil samples may be collected using direct push samplers, split-barrel samplers, thin-wall samplers or roto-sonic drilling. In the event of obstructions, samples should be collected as close as possible to the original prescribed sampling location. Minimum clearances may apply if utilities are located in proximity to drilling operations. Precautions should be taken to avoid contamination among

samples, for example the use of new disposable gloves with each sample and decontamination of non-disposable equipment in accordance with SOP 016. Obvious background or high concentration samples should be segregated. The specific sampling techniques will vary by the analyte of interest and depth below ground surface. QA/QC is verified by accurate labelling information, field log and data sheets, and COC forms. Detailed descriptions of the sampling methods for soils are found in SOP No. 008 and SOP No. 009.

Groundwater: Groundwater sampling locations are identified on project-specific documents, and the actual sampling location should be as close as possible to the original approved site. Efforts should be made to ensure the sample is representative of the target depth. Pumping is the most common method of well purging and sample collection, and various types of pumps may be used depending on the sampling location and specific equipment limitations. Following installation, wells will be developed using portable submersible of air-lift pumps in accordance with SOP No. 018. If the water table is shallow, then suction-lift (peristatic) pumps will be used for purging and sample collection. If the water table is deeper than the capability of a suction lift pump, then a portable submersible pump will be used for purging and sample collection. . Wells will be purged and sampled using the low-flow groundwater sampling method in accordance with SOP No. 007.. After extraction from the well, some samples may require filtration or preservatives before cold storage. QA/QC is verified by accurate labelling information, field log and data sheets, and COC forms. Detailed descriptions of the sampling methods for groundwater are found in SOP No. 006 and SOP No. 007. Precautions should be taken to avoid contamination among samples, for example the use of new disposable gloves with each sample and decontamination of non-disposable equipment in accordance with SOP No. 016.

Surface Waters: Surface water sampling locations are identified on project work plans, and the field sampling should be completed as close as possible to the approved site. The locations should be based on a prior understanding of the hydrology of the water body and analyte of interest, in order to produce a representative sample within the target zone. Depending on these factors, the sample may be gathered across several depths by multiple methods, including dip sampling, or direct sampling. QA/QC is verified by accurate labelling information, field log and data sheets, and COC forms. Detailed descriptions of the sampling methods for surface waters are found in SOP No. 004. Precautions should be taken to avoid contamination among samples, for example the use of new disposable gloves with each sample and decontamination of non-disposable equipment in accordance with SOP No. 016.

Soil Gas: Soil gas samples will be collected at the locations provided in the approved work plan, or as close as possible to the original sites. Gas sampling ports may be installed through concrete or asphalt slabs using appropriate hand equipment. Following port installation, leak testing will be conducted to ensure the integrity of each port. Prior to sample collection, purging below the slab is completed using a syringe and three way valve. Samples may be collected in Summa canisters once the purging procedure is completed. Samples will be collected over at least an 8-hour period using a flow regulator. QA/QC is verified by accurate labelling information, field log and data sheets, and COC forms. Following the collection of samples, temporary soil gas monitoring points shall be abandoned in accordance with the requirements of COMAR 26.04.04.36. Detailed descriptions of the sampling methods for soil gas are found in SOP No. 002. Precautions should be taken to avoid contamination among samples, for example the use of new disposable gloves with each sample and decontamination of non-disposable equipment in accordance with SOP No. 016.

Sediments: Sediment samples are described as mineral or organic materials beneath an overlying aqueous layer such as a lake, pond, river, or stream. The samples should be gathered as close as possible to the original locations identified in the project work plan. Among other factors, the overlying flow regime, sediment physical characteristics, and analyte identity should be considered while selecting the sampling location. Depending on the sampling goals and sediment depths below the surface, the procedure may be completed using either hand-held or mechanized equipment. Several techniques are possible depending on the characteristics of the sampling zone. Sampling techniques may utilize a Thin-Wall Tube Auger, Ponar Dredge, or a suction sampler depending on the depth of water and the thickness and consistency of sediments. QA/QC is verified by accurate labelling information, field log and data sheets, and COC forms. Detailed descriptions of the sampling methods for sediments are found in SOP No. 003. Precautions should be taken to avoid contamination among samples, for example the use of new disposable gloves with each sample and decontamination of non-disposable equipment in accordance with SOP No. 016.

QAPP Worksheet #19 & 30: Sample Containers, Preservation, and Hold Times
(UFP-QAPP Manual Section 3.1.2.2)
(EPA 2106-G-05 Section 2.3.2)

Laboratory: Pace Analytical Services **Contact:** Justin Hall **Address:** 1638 Roseytown Road, Suites 2, 3, and 4, Greensburg, PA 15601
Email: justin.hall@pacelabs.com **Phone:** (717) 377-5423
List any required accreditations/certifications:
Back-up Laboratory: Caliber Analytical Services, LLC
Sample Delivery Method: Courier/FedEx

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Volatile Organic Compounds (VOCs)	Soil	8260B and EPA5035A / *PGH-O-015-9*	3/31/2016	3 – (1) 60-ml septum sealed glass vial for screening, dry weight determination; (2) 40-ml VOA vials w/ PTFE-faced silicone septum, DI water and stir bar	Freeze	48 hours	14 days	10 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Semi-Volatile Organic Compounds (SVOCs)/Polyaromatic Hydrocarbons (PAHs)	Soil	8270D and 8270D SIM / *PGH-O-001-9 and PGH-O-023-5*	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C	14 days	40 days	10 days
Total Petroleum Hydrocarbons (TPH) – Diesel Range Organics (DRO)/Gasoline Range Organics(GRO)	Soil	8015B and 8015C Modified / *WI-PGH-O-003-0 and WI-PGH-O-002-0*	3/31/2016	GRO: 3 – (1) 60-ml septum sealed glass vial for screening, dry weight determination; (2) 40-ml VOA vials w/ PTFE-faced silicone septum DRO: 4 oz jar	4 ± 2°C GRO: CH_3OH/ $NaHSO_4$	14 days	14 days – GRO 40 days – DRO	10 days
Polychlorinated Biphenyls (PCBs)	Soil	8082/ *NY-O-314-rev.04*	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C Protected from light	14 days	365 days	10 days
Dioxins and Furans	Soil	8290/S-MN-H-001	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C	30 days	40 days	10 days
Target Analyte List (TAL) Metals	Soil	6010C and 3050B/ *PGH-M-013-7 and PGH-M-008-16*	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C	28 days	180 days	10 days
Mercury	Soil	7470A/ *PGH-M-017-5*	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C	28 days	28 days	10 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Chromium VI	Soil	7196A/ *PGH-I-012-10 and PGH-I-066-1*	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C	28 days	28 days	10 days
Cyanide	Soil	9012A/ *PGH-I-053-12*	3/31/2016	1 250 ml Amber Glass Jar	4 ± 2°C	14 days	14 days	10 days
pH	Soil	9045D / *PGH-I-003-5*	3/31/2016	1 250 mL Amber Glass Jar	4 ± 2°C	ASAP	ASAP	10 days
VOCs	GW	8260B and EPA5030B / *PGH-O-015-9*	3/31/2016	3 – (3) 40-ml VOA vials w/ PTFE-faced silicone septum	4 ± 2°C HCl	14 days	14 days	10 days
SVOCS/PAHs	GW	8270D and 8270D SIM / *PGH-O-001-9 and PGH-O-023-5*	3/31/2016	1 Liter Amber Glass	4 ± 2°C	7 days	40 days	10 days
TPH–DRO/GRO	GW	8015B and 8015C Modified / *WI-PGH-O-003-0 and WI-PGH-O-002-0*	3/31/2016	GRO: 3 – 40-ml VOA vials w/ PTFE-faced silicone septum DRO: 1Liter Amber Glass	4 ± 2°C GRO: HCl	14 days – GRO 7 days – DRO	14 days – GRO 40 days – DRO	10 days
PCBs by GC/MS	GW	680 / *S-NY-O-040-rev. 08*	3/31/2016	1 Liter Amber Glass	4 ± 2°C Protected from light	14 days	365 days	10 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Target Analyte List Metals	GW	6010C / *PGH-M-008-16 and PGH-M-015-8*	3/31/2016	1 250 ml Plastic	4 ± 2°C HNO_3	28 days	180 days	10 days
Mercury	GW	7470A / *PGH-M-017-5 PGH-M-011-6*	3/31/2016	1 250 ml Plastic	4 ± 2°C HNO_3	28 days	28 days	10 days
Chromium VI	GW	7196A / *PGH-I-012-10*	3/31/2016	1 250 ml Plastic	4 ± 2°C	24 hours	24 hours	10 days
Alkalinity	GW	SM 2320B / *PGH-I-015-7*	3/31/2016	1 250 Plastic	4 ± 2°C	14 days	14 days	10 days
BOD	GW	SM 5210 B / *PGH-I-009-10*	3/31/2016	1 – 1 L Plastic	4 ± 2°C	48 hours	48 hours	10 days
COD	GW	Hach 8000 / *PGH-I-033-6*	3/31/2016	50 ml Glass	4 ± 2°C H_2SO_4	28 days	28 days	10 days
Cyanide	GW	9012A / *PGH-I-053-12*	3/31/2016	1 250 ml Plastic	4 ± 2°C NaOH	14 days	14 days	10 days
Ferrous Iron	GW	SM-3500 / *PGH-I-058-4*	3/31/2016	1 40 mL Amber	None	Analyze Immediately	Analyze Immediately	10 days
Oxygen, Dissolved	GW	360.1 / *PGH-I-045-5*	3/31/2016	500 ml Plastic or Glass bottle, with Glass top	None	Analyze Immediately	Analyze Immediately	10 days
Sulfate, Nitrate, and Chloride	GW	EPA 300 / *PGH-I-059-7*	3/31/2016	1 500 ml Plastic	4 ± 2°C	28 days	28 days	10 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Sulfide	GW	SM 4500-S D / PGH-I-010-5	3/31/2016	1 500 ml Plastic	4 ± 2°C	Analyze Immediately	Analyze Immediately	10 days
Total Organic Carbon	GW	5310B / PGH-I-060-6	3/31/2016	1 40 mL Amber Glass	4 ± 2°C H_2SO_4	28 days	28 days	10 days
Total Dissolved Solids	GW	160.1 / PGH-I-020-9	3/31/2016	1 250 ml Plastic	4 ± 2°C	7 days	7 days	10 days
VOCs	AIR	TO-15 / *S-LI-O-022-rev.01*	12/15/2015	1 Summa ® Cannister	None	28 days	28 days	10 days
Mercury Vapor	AIR	*NIOSH 6009 HGAVAPOR*	3/31/2016	Sorbent Tube	None	28 days	28 days	10 days
Oil and Grease	GW	1664A / *PGH-I-042-08*	3/31/2016	1 – 1L Glass	4 ± 2°C HCl	28 days	28 days	10 days
HEM and SGT-HEM	Soil	9071B / *PGH-I-052-7*	3/31/2016	1 250mL Glass	None	28 days	28 days	10 days

QAPP Worksheet #20: Field QC Summary
(UFP-QAPP Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Section 2.3.5)

Analyte/Analytical Group	Matrix	Number of Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equipment Blanks	Trip Blanks	Other	Total Number Analyses
Volatile Organic Compounds (VOCs)	Soil	TBD	1/20	1/20	1/20	1/20	1/20	1 per day	NA	TBD
Semi-Volatile Organic Compounds (SVOCs)/Polyaromatic Hydrocarbons (PAHs)	Soil	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Total Petroleum Hydrocarbons (TPH) – Diesel Range Organics (DRO)/Gasoline Range Organics(GRO)	Soil	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Oil & Grease (O&G)	Soil	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Polychlorinated Biphenyls (PCBs)	Soil	TBD	1/20	1/20	1/20	NA*	NA*	NA	NA	TBD
Target Analyte List (TAL) Metals	Soil	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Mercury	Soil	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Chromium VI	Soil	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Cyanide	Soil	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
pH	Soil	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD

Analyte/Analytical Group	Matrix	Number of Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equipment Blanks	Trip Blanks	Other	Total Number Analyses
VOCs	GW	TBD	1/20	1/20	1/20	1/20	1/20	1 per day	NA	TBD
SVOCS/PAHs	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
TPH–DRO/GRO	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
O&G	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
PCBs	GW	TBD	1/20	1/20	1/20	NA*	NA*	NA	NA	TBD
TAL Metals	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Mercury	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Chromium VI	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Alkalinity	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
BOD	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
COD	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
Cyanide	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
Ferrous Iron	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Oxygen, Dissolved	GW	TBD	1/20	1/20	1/20	1/20	1/20	NA	NA	TBD
Sulfate, Nitrate, and Chloride	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
Sulfide	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
Total Organic Carbon	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
Total Dissolved Solids	GW	TBD	1/20	NA	NA	1/20	1/20	NA	NA	TBD
VOCs	AIR	TBD	NA	NA	NA	1/20	1/20	NA	NA	TBD

Analyte – The substance whose chemical constituents are being identified and measured.
Matrix - The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.
Field Duplicate - Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.
Matrix Spike - An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix
Matrix Spike Duplicate - Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.
Field Blank - A sample of analyte free water poured into the container in the field, preserved and shipped to the laboratory with field samples.
Equipment Blank - A sample of analyte free water poured over or through decontaminated field sampling equipment prior to the collection of environmental samples.
Trip Blank - A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

*Per the 10/1/15 email from EPA, Field and Equipment Blanks will not be analyzed for PCBs

QAPP Worksheet #21: Field SOPs
(UFP-QAPP Manual Section 3.1.2)
(EPA 2106-G-05 Section 2.3.2)

This worksheet is intended for use to document the specific field procedures being implemented, which is important for measurement traceability. The QAPP must contain detailed descriptions of procedures for all field activities, including sample collection; sample preservation; equipment cleaning and decontamination; equipment testing, maintenance and inspection; and sample handling and custody. These procedures are included in the SOPs listed below. If an SOP provides more than one procedure or option (for example, one SOP covers the use of several different types of field equipment for the same procedure), individual work plans will note the specific option or equipment being used. The SOPs are included in Appendix B of the QAPP. Field SOPs must be readily available to all field personnel responsible for their implementation.

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 001	Indoor Air Sampling, Revision 3, 9/4/2015	EAG	Collection of an indoor air sample from a potential tenant space or enclosure	N	
SOP 002	Sub-Slab Soil Gas Sampling, Revision 4, 9/4/2015	EAG	Installation and collection of soil gas sample	N	
SOP 003	Sediment Sampling, Revision 2, 8/27/2015	EAG	Collection of a sediment sample for discrete and composite samples	Y	
SOP 004	Surface Water Sampling, Revision 2, 8/27/2015	EAG	Collection of surface water samples from shallow streams, temporary flows, and large and small surface water bodies.	N	

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 005	Management of Investigation-Derived Wastes, Revision 2, 9/1/2015	EAG	Management of all on-site derived waste including: soil, water, PPE, and miscellaneous debris	Y	
SOP 006	Groundwater Sampling, Revision 3, 8/27/2015	EAG	Groundwater sampling at temporary points using non-dedicated equipment	Y	See Low-Flow Sampling SOP 007
SOP 007	Groundwater Low-Flow Sampling, Revision 3, 9/1/2015	EAG	Groundwater Sampling at temporary and permanent monitoring locations	Y	Decontamination of pH and specific conductance meters and thermometers
SOP 008	Surface Soil Sampling, Revision 4, 10/2/2015	EAG	Collection of soil samples representative of the soil surface	Y	
SOP 009	Subsurface Soil Sampling, Revision 3, 10/2/2015	EAG	Collection and identification of representative subsurface soil samples from borings	Y	
SOP 010	Field Logbook, Revision 3, 10/2/2015	EAG	Procedure and requirements for entering information in a field logbook	Y	
SOP 011	Sample Handling, Packing, Shipping and Chain-of-Custody, Revision 2, 8/28/2015	EAG	Procedure and requirements for sample management, including chain-of-custody, handling, packing, and shipping	Y	

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 012	Geologic Logging, Revision 1, 10/2/2015	EAG	Logging geologic descriptions of soil and rock samples during the drilling of boreholes and installation of wells or piezometers	Y	
SOP 013	Soil Boring Methods, Revision 0, April 2015	EAG	Guidelines for performing soil borings	Y	
SOP 014	Monitoring Well Construction, Revision 2, 10/2/2015	EAG	Construction of groundwater monitoring wells in unconsolidated formations	Y	
SOP 015	Test Pitting, Revision 3, 9/3/2015	EAG	Procedures for test pitting and collection of representative soil samples from the pit faces.	Y	
SOP 016	Equipment Decontamination, Revision 2, 9/1/2015	EAG	On-site decontamination of sampling equipment, heavy equipment, and personal protective equipment	Y	
SOP 017	Calibration of Field Instruments, Revision 3, 10/2/2015	EAG	Framework for calibrating field instruments	Y	
SOP 018	Well Development, Revision 0, April 2015	EAG	Developing monitoring wells or extraction wells, following installation but prior to designated use	Y	

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 019	Depth to Groundwater and NAPL Measurements, Revision 0, April 2015	EAG	Determining depth to groundwater, determining depth and apparent thickness of non-aqueous phase liquid	Y	
SOP 020	Field Location of Sample Points, Revision 2, 8/31/2015	EAG	Translating proposed sample locations shown in work scopes to actual sample locations in the field	Y	
SOP 021	In-Situ Hydraulic Conductivity Testing, Revision 1, 8/14/2015	EAG	Conducting permeability tests during hydrogeological studies	Y	
SOP 022	Aquifer Pumping Tests, Revision 1, 8/14/2015	EAG	Conducting aquifer pumping tests	Y	
SOP 023	X-Ray Fluorescence Procedures, Revision 2, 8/31/2015	EAG	Methods used for performing lead-based paint inspections to determine if lead-based paint is present and in which components of the building	Y	
SOP 024	Electronic Data Deliverables for Laboratory Analytical Data, Revision 1, 8/14/2015	EAG	Description of documentation, formatting and submission of electronic laboratory analytical data.	Y	

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP 025	Niosh Method 6009 Sample Collection, Revision 2, 8/30/2015	EAG	Collection of air samples to be analyzed for mercury	Y	
SOP 026	Photoionization Detector, Revision 1, 10/2/2015	EAG	Using a photoionization detector to detect a variety of chemical compounds in air, both organic and inorganic	Y	
SOP 027	Turbidimeters, Revision 3, 10/2/2015	EAG	Calibrating and using turbidimeters used to measure water quality parameter of turbidity	Y	
SOP 028	Direct Push Installation and Construction of Temporary Groundwater Sample Collection Points, Revision 1, 10/2/2015	EAG	Procedures for the proper installation and construction of temporary Direct Push Groundwater Sample Collection Points in unconsolidated formations	Y	

QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection
(UFP-QAPP Manual Section 3.1.2.4)
(EPA 2106-G-05 Section 2.3.6)

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Gas Vapor Probe Kit	AMS	NA	Return to supplier for repair or replacement if damaged or not functioning	Check if equipment is clean and survey the site for objects underground.	Prior to use.	Sample obtained	Decontaminate or replace probe kit	Field Personnel	SOP 002
AMS Soil Core Sampler	AMS	NA	Return to supplier for repair or replacement if damaged or not functioning	Ensure equipment is clean and decontaminated. Particularly treads and top cap vent	Prior to each use.	Sample obtained	Decontaminate or replace core sampler	Field Personnel	SOP 009
Large Bore Soil Sampler	Geoprobe	NA	Return to supplier for repair or replacement if damaged or not functioning	Ensure all parts are present and sampler is properly assembled and decontaminated.	Prior to each use.	Sampler is properly assembled and probe successfully recovers a soil sample	If assembled incorrectly, reassemble sampler. If parts are broken, contact manufacturer for replacements.	Field Personnel	Technical Bulletin No. 93660 SOP 008 SOP 009

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
PRT System Operation Soil Gas Sampling	Geoprobe	NA	Replace if damaged or not functioning	Check tubing is properly attached and PRT probe is properly assembled. Ensure PRT Adapter functions properly.	Prior to each use.	PRT system successfully recovers a soil gas sample.	If parts are broken or missing, contact manufacturer for replacements.	Field Personnel	Soil Gas Sampling-PRT System Operation SOP 002
Soil Gas Implants Operation	Geoprobe	NA	Replace if damaged or not functioning	Ensure implants are not broken, ensure that tubing is properly attached to the implants	Prior to each use.	Implant is stable and the tubing is properly attached while leaving enough length to take a sample	If implant is broken, contact the manufacturer for a new one. If tubing is attached incorrectly, it can be reattached or a longer tube can be implemented.	Field Personnel	Implants Operation from Geoprobe Systems SOP 002

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Bladder Pumps	Geotech	NA	Follow Chapter 4-System Maintenance of the equipment manual. Disassemble the bladder pump, decontaminate and replace key components as needed and reassemble. Return to supplier for repair if damaged or not functioning.	Follow safety procedures when attaching pump, check system components, calculate air consumption, ensure tubing is straight and not bent due to prior coiling.	Varies by site, but on a regular schedule	Pump is active	Follow system troubleshooting in operation manual	Field Personnel	SOP 006 SOP 007
Geotech Controller	Geotech/ 300PSI Geotech/ 500PSI	NA	Return to supplier for repair or replacement if damaged or not functioning	Determine power source, select air source, check system components	Prior to use.	Controller is functional	Follow instructions provided in Section 5 – "System Troubleshooting" in operation manual	Field Personnel	SOP 006 SOP 007
DC to AC Inverter	Geotech	NA	Return to supplier for repair or replacement if damaged or not functioning	Check for frayed wires and physical damage	Prior to use.	Power is converted	Troubleshoot connection status or contact manufacturer	Field Personnel	
Disposafilter Capsules	Geotech	NA	Replace if damaged or not functioning	Check for physical damage	Prior to use.	Capsules hold the samples	Get new capsules if broken	Field Personnel	

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Water Level Meter	Geotech/ ET Heron Skinny Dipper Solinst/ Model 101 Solinst/ Model 102	NA	Refer to maintenance and care sections of equipment manuals. Replace battery when needed and clean the conductivity contact of probe periodically. Return to supplier for repair or replacement if damaged or not functioning	Check battery charge, check if equipment is clean (especially probe), check light and buzzer work, check for physical damage	Prior to each use.	Probe returns reading	Follow troubleshooting protocol, and if problem persists contact manufacturer or buy new meter	Field Personnel	SOP 019
Geocontrol PRO Bladder Pump Controller	Geotech	NA	Return to supplier for any required service. Use damp cloth to remove caked on diret and dust from the exterior surface. Do not soak or directly spray liquids on the Geocontrol PRO	Check fuse and amperage, check battery, check for physical damage	Prior to use.	Controller is functional	Perform basic troubleshooting procedures, but Maintenance and repair should be performed by Geotech technicians	Field Personnel	SOP 006 SOP 007

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
SS geosub and Controller	Geotech	NA	Refer to Section 4- "System Maintenance" of equipment manual. Clean the controller as needed with mild soap and water on a cloth, do not spray water or any other liquid or pressurized solvents. Use an air source to blow water out of all cable connections as needed. Clean the pump between sampling events using detergent and water. Return to supplier for any required service	Check electrical connections and power sources, check for physical damage, check display for any messages	Prior to use.	Controller is functional	Perform basic troubleshooting procedures outline in manual, or call Geotech Technical Support	Field Personnel	SOP 006 SOP 007

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Redi-Flo Pump	Grundfos/ 2 & 4	NA	Refer to Maintenance section of equipment manual. Periodically inspect Redi-Flo components. If pump is operating at a decreased capacity and the impeller assembly components do not appear to be the cause, the motor should be checked following the checklist supplied in the equipment manual. Return to the supplier for any required service.	Check electrical connections and power sources, check for physical damage to pump and connected wires.	Prior to use.	Pump is functional	Follow manual's procedure for dismantling and reassembling and other corrective features	Field Personnel	SOP 006 SOP 007
RediFlo VFD	Grunfos	NA	Return to supplier for repair or replacement if damaged or not functioning	Follow outlined precautions to avoid electric shock, check for physical damage,	Prior to use, and occasional visual inspection	Fault Message says "no fault exists" and system is functional	View event log and fault messages and take corresponding action, or send in for repair	Field Personnel	SOP 006 SOP 007

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Turbidity Meter	Hach/ 2100Q Hach/ 2100Qis LaMotte/ Kit LaMotte/ 2020 we-wi	3 Point Calibration-StablCal Standard Reference SOP 017 (or SOP 027) for more information	Return to supplier for repair or servicing. Periodic cleaning of the exterior housing should be done with a damp, lint-free cloth. The light chamber and optics area should be cleaned using a can of pressurized air, and/or a cotton swab dampened with Windex®.	Clean meter, check battery, set-up sample ID tag to associate readings with sample location	Prior to each use.	Value appears with no error or warning message	Follow basic troubleshooting procedures, or replace turbidity meter if necessary	Field Personnel	SOP 027

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Multi Parameter Meters	Horiba/ Flow Through Cell U-50 Series Horiba/ Water Quality Meter U-50 Series YSI/Proplus	Reference SOP 017	Refer to Maintenance sections of equipment manuals. Clean components as part of routine care. Inspect O-rings for contamination and clean or replace, if necessary. Do not over-grease O-rings. Sensor specific cleaning and maintenance should be performed in accordance with specific instructions provided in the manual. Return to supplier for any required servicing.	Inspect optics and probes for external damage	Prior to each use, and when unstable readings obtained	Stable reading with no drift unless monitoring occurs continuously over a given time period.	Recalibrate the device in accordance to SOP 17. If probe is damaged, return to manufacturer.	Field Personnel	SOP 004 SOP 005 SOP 006 SOP 007 SOP 017

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
INNOV-X Systems XRF Meter	INNOV-X Systems	Calibrated in the factory. Reference SOP 023	Return to supplier for repair or replacement if damaged or not functioning.	Ensure battery is charged. Check warning lights. Ensure accompanying HP iPAQ is properly functioning.	Prior to each use	iPAQ is properly functioning and the meter's warning lights are off.	If there are errors, turn the meter off and then on again to see if the warming lights appear. If they do, contact the manufacturer regarding the issue.	Field Personnel	SOP 023
Pressure Transducer	Solinst/ Levelogger Model 3001	NA	Return to supplier for repair or replacement if damaged or not functioning.	Perform visual inspection and ensure screw cap is intact	Prior to each use	Device is properly installed to desired depth and functioning	Send to supplier for repair/ replacement	Field Personnel	SOP 022

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
PID Meter	MiniRAE 3000	See SOP 026. See instruction manual.	Cleaning of the sensor components is not typically required.. Follow sensor cleaning procedures outlined in user's guide using GC grade methanol if requried. The lamp housing may require cleaning or the lamp may require replacement. Never use water solutions to clean the lamp, never touch the window surface with anything that may leave a film. Clean as outlined in the user's guide. Cleaning of the instrument should be performed with a soft dry cloth. Return to supplier for any required service.	Check battery, ensure no warning lights or alarm signals are active. Ensure there is no external damage to the device.	Prior to each use.	Device functions, no warning lights appear, and a stable reading is taken. External damage not present.	Refer to the troubleshooting section of the operator's manual. Contact the manufacturer for problems not in the troubleshooting section of the operator's manual.	Field personnel	SOP 026

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
1.66 inch Bladder Pump	Solinst/ Model 407	NA	Return to supplier for repair or replacement if damaged or not functioning	Check operating pressure does not exceed 250psi, and that SOP 016 procedure was followed	Prior to use.	Disassemble Pump, wash all components with phosphate free soap or detergent, rinse with deionized water, if needed replace worn O-rings and Bladder, and reassemble	If pump is assembled incorrectly, take it apart and reassemble in accordance to the guide in the operator manual. If functioning incorrectly, contact manufacturer for another.	Field Personnel	SOP 006 SOP 007
Solinst 1.66 inch Double Valve Pump Model 408	Solinst/ Model 408	NA	Return to supplier for repair or replacement if damaged or not functioning	Ensure that there is no external damage to the pump and that connections between parts are properly made. Determine that SOP 016 procedure was followed	Prior to use.	Pump is decontaminated in accordance to the operator's manual and all connections are properly made between parts.	If pump is assembled incorrectly, take it apart and reassemble in accordance to the guide in the operator manual. If functioning incorrectly, contact manufacturer for another.	Field Personnel	SOP 006 SOP 007
Solinst Disposable Filters Model 860	Solinst/ Model 860	NA	Replace if damaged or not functioning	Ensure filter is not cracked or broken	Prior to each use.	Filter is not cracked or broken.	Buy another from the manufacturer	Field Personnel	SOP 006 SOP 007

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Solinst Electronic Pump Control Unit Model 464	Solinst/ Model 464	NA	Refer to Section 4 – Maintenance of equipment manual. Compressed air should be sent through control unit after each sampling session. Return to supplier for repair or replacement if damaged or not functioning.	Inspect for external damage to LCD screen, air valves and pressure gauge.	Prior to each use.	No external damage to the unit is present. Battery is charged and manual control works.	Recharge the battery if manual control is to be avoided. If unit is faulty, contact the manufacturer for another.	Field Personnel	SOP 006 SOP 007
Peristaltic Pump	Solinst/ Model 410	NA	Return to supplier for any required service.	Inspect for external damage to pump and proper tubing installation, change out silicon tubing if needed, check motor. Make sure tubing is properly sized to fit the pump.	Prior to each use. Motor should be checked every 7-8 hours for overheating.	Pump tubing is properly installed and pump is attached to a proper power source	If tubing is damaged, replace the tubing. The pump should adequately perform its task and if motor damage is present, buy another from the manufacturer.	Field Personnel	SOP 006

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Interface Meter	Solinst/ Model 122	NA	Refer to cleaning and maintenance section of equipment manual. PVDF tape and probe should be cleaned after each use. Return to supplier for repair or replacement if damaged or not functioning.	Ensure that reel turns and that probe is functional using visual and audio signals, check battery, follow equipment check in operator's manual	Prior to each use.	Probe returns a reading once it makes contact with water.	Buy replacement parts from the manufacturer and replace them. Follow troubleshooting guide in operator's manual.	Field Personnel	SOP 019
Tag Line	Solinst/ Model 103	NA	Refer to routine care section of equipment manual. Weight and tape should be cleaned after use. Return to supplier for repair or replacement if damaged.	Ensure reel turns and that weight is attached to the cable, perform equipment check in operator's manual	Prior to each use.	Device turns to release weight, and an accurate measurement can be made.	Buy replacement parts from the manufacturer and replace them.	Field Personnel	SOP 019
GPS Location Device	Trimble/ Geo 7 Series Trimble/ Pathfinder ProXRT Receiver Trimble/ Pro Series Receivers	NA	Return to supplier for repair or replacement if damaged or not functioning	Ensure receiver and connectivity features are functional, check for physical damage, check battery charge	Prior to each use.	Receiver, connectivity, and LCD Screen are functional. Device turns on.	Reset the Receiver. If necessary, charge the battery of the device.	Field personnel	SOP 020

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Standard/ Petite Ponar Grab Dredge	Wildlife Supply Company	NA	Refer to Maintenance section of equipment manual. Clean equipment adequately, and return to supplier for repair or replacement if damaged or not functioning	Check for external damage and contamination	Prior to use.	Dredge opens and closes properly.	Return to manufacturer/ rental facility and buy a new dredge.	Field Personnel	SOP 003
Summa Canister	Laboratory provided and certified	Certified by Laboratory	Return to laboratory for replacement if damaged	Check for external damage	Prior to mobilization	Vacuum gauge holds constant value.	Return to laboratory and request another	Field Personnel	SOP 001 SOP 002
Gas Flow Controller/ Filter	Laboratory provided and certified	NA	Return to laboratory for replacement if damaged	Check for gas leaks in both the gauge and the filter.	Prior to sample collection.	Filter and gauge do not show signs of leaking. Gauge holds a constant reading.	Return to laboratory and request another set.	Field Personnel	SOP 001 SOP 002
Core/ Hammer Rotary Drill	Varies	NA	Return to supplier for repair or replacement if damaged	Ensure bit is not bent and is not dulled. Ensure bit is properly attached to drill.	Prior to use	Bit is properly secured and in good condition.	Return to manufacturer/ rental facility and buy a new unit.	Field Personnel	SOP 001

Field Equipment	Manufacturer/ Model	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Dip Sampler	Varies, e.g., Nasco, Cole-Parmer	NA	Return to supplier for repair or replacement if damaged	Ensure sampling stick holds sampling container snugly. Ensure that there are no cracks in the container.	Prior to sample collection	Container has no cracks. Unit has no external damage.	Replace	Field Personnel	SOP 004
Stainless Steel Bucket Auger	Varies	NA	Decontaminate after each use. Use teflon tape around threads	Check for external damage and contamination	Prior to use	Bucket retains structural identity	Replace	Field Personnel	SOP 008 SOP 009
Roto Sonic Drilling Equipment	Varies, provided by drilling subcontractor	NA	Replace or repair if damaged	Check for external damage and contamination.	Prior to usage	Drilling Equipment	Return to manufacturer/ rental facility and request another unit	Field Personnel	SOP 008 SOP 009
Split-spoon Soil Sampler	Varies, provided by drilling subcontractor	NA	Replace or Repair if damaged	Check for external damage and contamination. Ensure drive tip is not dented.	Prior to taking samples	Cutting shoe is not broken and sampler functions normally	Replace	Field Personnel	SOP 008 SOP 009
Shelby Tube/Thin-walled Soil Sampler	Varies, provided by drilling subcontractor	NA	Replace or repair if damaged	Check for external damage and contamination. Ensure sampler is not dented.	Prior to taking samples	Cutting shoe is not broken and sampler functions normally	Return to manufacturer/ rental facility and buy a new sampler.	Field Personnel	SOP 008 SOP 009
Macroprobe /Direct Push Soil Sampler	Geoprobe	NA	Return to supplier for repair or replacement if damaged	Check for external damage and contamination	Prior to taking samples	Cutting shoe is not broken and sampler functions normally	Return to manufacturer/ rental facility and buy a new sampler.	Field Personnel	SOP 008 SOP 009

QAPP Worksheet #23: Analytical SOP's
(UFP-QAPP Manual Section 3.2.1)
(EPA 2106-G-05 Section 2.3.4)

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	‡Modified for Project? Y/N
S-LI-O-022-rev.01	*Analysis of Volatile Organics in Ambient Air Using Summa or Other Specially Prepared Canisters by GC/MS 8/17/2015, rev. 01*	Definitive	Air/VOCs	GC/MS	N
PGH-O-015-9	*Volatile Organic Compounds, Methods: EPA 8260B & 8260C, 8/14/2015, rev. 9*	Definitive	Soil & Aqueous/VOCs	GC/MS	N
PGH-O-001-9	*Analysis of Semivolatiles by GCMS, Methods: EPA 8270C & 8270D, 8/19/2015, rev.9*	Definitive	Soil & Aqueous/SVOCs	GC/MS	N
PGH-O-023-5	*Polyaromatic Hydrocarbons by Selective Ion Monitoring (PAHS by SIM), EPA Method 8270C SIM & 8270D SIM, 7/12/2014, rev. 5*	Definitive	Soil & Aqueous/SVOCs	GC/MS SIM	N
WI-PGH-O-003-0	*Work Instruction for Gasoline Range Organics (GRO), Methods: EPA 8015B, 8/14/2015*	Definitive	Soil & Aqueous/GRO	GC	Y, Modification to address EPA comments on PGH-O-016-8
WI-PGH-O-002-0	*Work Instruction for Diesel Range Organics (DRO), Methods: EPA 8015B, 8/14/2015*	Definitive	Soil & Aqueous/DRO	GC	Y, Modification to address EPA comments on PGH-O-004-7
S-NY-O-314-rev.04	*Determination of Polychlorinated Biphenyls (PCBs) Aroclors, Reference Method: EPA Method 8082A, 02/06/2016*	Definitive	Soil/PCBs	GC	Y, Modification to address EPA comments on PGH-O-004-7
S-NY-O-040-rev.08 - PCBs by GCMS - FINAL	*Analysis of PCBs by GC/MS, Reference Methods: EPA Method 680, 8/14/2015, rev.8*	Definitive	Aqueous/PCBs	GC/MS	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	‡Modified for Project? Y/N
PGH-M-015-8	*Preparation of Aqueous Samples for ICP Analysis, Method 3005A, 7/15/2014, rev.8*	Definitive	Aqueous/ICP Metals	ICP	N
PGH-M-013-7	*Preparation Solid/ Semi Solid Samples for ICP Analysis, Method: 3050B, 7/15/2014, rev.7*	Definitive	Soil/ICP Metals	ICP	N
PGH-M-008-16	*Metals and Trace Elements in Waters, Wastes and Solids by ICP-AES by EPA Methods 200.7, 6010B and 6010C, 7/7/2015, rev.16*	Definitive	Soil & Aqueous/ICP Metals	ICP	N
PGH-M-012-8	*Digestion of Solid Samples for Mercury Analysis, Methods: EPA 7471A & 7471B, 7/13/2014, rev.8*	Definitive	Soil/Mercury	CVAA	N
PGH-M-011-6	*Digestion of Aqueous Samples for Mercury Analysis, Methods: EPA 245.1 and 7470A, 7/13/2014, rev.6*	Definitive	Aqueous/Mercury	CVAA	N
PGH-M-017-5	*Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy (Cetac), Methods: EPA 245.1, 7470A, 7471A and 7471B, 7/13/2014, rev.5*	Definitive	Soil & Aqueous /Mercury	CVAA	N
HGVAPOR	*Mercury Vapor in Atmospheres, 3/2/2015, rev.2*	Definitive	Air/Mercury	CVAA	N
PGH-I-053-12	*Cyanide; Free, Total, and Amenable, Methods: EPA 335.4, EPA 9010C, 9012B, 9013, 9014 and SM 4500-CN- A., B., C., E., G., and I., 3/10/2015, rev.12*	Definitive	Soil & Aqueous /Cyanide	SmartChem® instrument	N
PGH-I-066-1	*Alkaline Digestion of Solid Samples for Hexavalent Chromium, Methods: EPA SW-846 3060A, 7/6/2015, rev. 1*	Definitive	Soil/Hexavalent Chromium	Spectrophotometer	N
PGH-I-012-10	*Hexavalent Chromium Analysis, Methods: SW 846 7196A, SM 3500-Cr B-2009 & SM-3500-Cr-D, 7/6/2014, rev.10*	Definitive	Soil & Aqueous/ Hexavalent Chromium	Spectrophotometer	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	‡Modified for Project? Y/N
PGH-I-042-8	*Gravimetric Determination of Oil and Grease in Water by Automated Solid Phase Extraction, Method 1664A, 10/16/2014, rev. 8*	Definitive	Aqueous/Oil and Grease	Gravimetric	N
PGH-I-052-7	*Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT-HEM) Analysis by Hexane Soxhlet Extraction, Method: 9071B, 7/11/2014, rev. 7*	Definitive	Soil/Oil and Grease	Gravimetric	N
PGH-I-015-7	*Alkalinity, Method SM 2320B, 7/11/2014, rev. 7*	Definitive	Aqueous	Titration	N
PGH-I-009-10	*Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand (BOD/CBOD), Method: SM 5210 B-2001, 7/10/2014, rev. 10*	Definitive	Aqueous	Incubation	N
PGH-I-033-6	*Chemical Oxygen Demand, Method: EPA 410.4, 4/23/2013, rev. 6*	Definitive	Aqueous	Spectrophotometer	N
PGH-I-058-4	*Ferrous Iron – Phenanthroline Method (SmartChem), Methods: SM 3500-Fe B(20th) / D(19th), 7/12/2014, rev. 4*	Definitive	Aqueous	Spectrophotometer	N
PGH-I-045-5	*Dissolved Oxygen, Membrane Electrode, (SM4500O-G), 7/11/2014, rev. 5*	Definitive	Aqueous	Membrane Electrode	N
PGH-I-059-7	*Inorganic Anions by Ion Chromatography, Method: EPA 300.0, 6/26/2015, rev. 7*	Definitive	Aqueous	Ion Chromatography	N
PGH-I-010-5	*Total Sulfide, SM 4500 S^{2-} F-2000, 7/10/2014, rev. 5*	Definitive	Aqueous	Titration	N
PGH-I-060-6	*Total Organic Carbon, Methods: SM 5310C and EPA 9060/9060A, 12/31/2014, rev. 6*	Definitive	Aqueous	Carbonaceous Analyzer	N
PGH-I-020-9	*Filterable Residue (Total Dissolved Solids), SM 2540 C-1997, 7/11/2014, rev. 9*	Definitive	Aqueous	Filtration	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	‡Modified for Project? Y/N
S-MN-H-001	*Preparation and Analysis of Samples For the Determination of Dioxins and Furans*	Definitive	Water, Sludge, Soil, Fly ash, Tissue, Food/food oil and waste materials	Varies	

‡ A brief summary of project-specific SOP modifications must be provided on this worksheet or referenced.

QAPP Worksheet #24: Analytical Instrument Calibration
(UFP-QAPP Manual Section 3.2.2)
(EPA 2106-G-05 Section 2.3.6)

Matrix: Soil Gas
Analytical Method: TO-15
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (TO-15)	Check of mass spectral ion intensities (tuning procedure) using BFB (TO-15)	Prior to ICAL and at the beginning of each 24-hour period.	Refer to method/SOP for specific ion criteria.	Retune instrument and verify.	Lab Manager / Analyst *	S-LI-O-022-rev.01
GC/MS (TO-15)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit. (ICAL)	Initial calibration prior to sample analysis	The %RSD for all calibrated target compounds must be ±30%.	Evaluate standards, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat initial calibration.	Lab Manager / Analyst *	S-LI-O-022-rev.01

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
			The area response for each internal standard in each calibration level must be within 40% of the mean area response over the calibration range. The relative retention time (RRT) of each compound must agree within ± 0.06 RRT units of the average RRT from the initial calibration curve.			S-LI-O-022-rev.01
GC/MS (TO-15)	Initial Calibration Verification (ICV)	Following the Initial Calibration	70-130%% for all target analytes. Analytes exceeding and associated data will be flagged and narrated.	Perform maintenance and repeat test. If system still fails, perform a new initial calibration.	Lab Manager / Analyst *	S-LI-O-022-rev.01
GC/MS (TO-15)	Continuing Calibration Verification (CCV)	Following an acceptable tune, and every 24 Hours during sample analysis.	70-130% for all target analytes. Analytes exceeding and associated data will be flagged and narrated. The RRT of each compound must agree within ± 0.06 RRT units of the average RRT from the initial calibration curve.	Perform maintenance and repeat test. If system still fails, perform a new initial calibration.	Lab Manager / Analyst *	S-LI-O-022-rev.01

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (TO-15)	Internal Standards (IS)	As each standard, blank and sample is being loaded	Retention time (RT) for blanks and samples must be within ±0.33 min of the RT for the ICAL and EICP areas within ±40% of the EICP area counts of the daily CCV	Inspect the system and reanalyze the blank. Analysis is discontinued until the blank meets the IS criteria. Also re-analyze any associated samples.	Lab Manager / Analyst *	S-LI-O-022-rev.01

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid/Aqueous
Analytical Method: 8260B
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (8260B)	Check of mass spectral ion intensities (tuning procedure) using BFB (8260B)	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method/SOP for specific ion criteria.	Retune instrument and verify.	Lab Manager / Analyst *	PGH-O-015-9
GC/MS (8260B)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit. (ICAL)	Initial calibration prior to sample analysis	Each analyte must meet one of the three options below: Option 1: RSD for each analyte ≤ 15%; Option 2: linear least squares regression for each analyte: r ≥ 0.99; Option 3: 2nd order curves such as quadratic the coefficient of determination (COD) (quadratic) for each analyte: r2 ≥ 0.99.	Evaluate standards, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat initial calibration.	Lab Manager / Analyst *	PGH-O-015-9

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
			% RSD CCCs 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride < 30. Min. RF of SPCCs 1,1-dichloroethane (0.10), bromoform (0.10), chlorobenzene (0.30), chloromethane (0.10) and 1,1,2,2-tetrachloroethane (0.30).			PGH-O-015-9
GC/MS (8260B)	Initial calibration verification (ICV)	Once after each ICAL	All project analytes within ±20% of true value.	Evaluate data. If problem (e.g., concentrated standard, plugged purge line) found, correct, then repeat second source verification. If it still fails, then repeat initial calibration.	Lab Manager / Analyst *	PGH-O-015-9
GC/MS (8260B)	Continuing calibration Standard (CCAL)	Following acceptable tune, prior to sample analysis and every 12 hours of analysis time.	1. Min RRF for SPCCs: 1,1-dichloroethane (0.10), bromoform (0.10), chlorobenzene (0.30), chloromethane (0.10) and 1,1,2,2-tetrachloroethane (0.30). 2. %Difference/%Drift for all1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride: %D < 20%. All other compounds %D <40%	Evaluate standard, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration.	Lab Manager / Analyst *	PGH-O-015-9

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (8260B)	Internal Standards	During acquisition of calibration standard.	Areas within -50% to +100% of last ICAL mid-point for each CCV ; The retention time shift for each internal standard must be within +/-30 seconds of its retention time in the most recent continuing calibration standard.	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning	Lab Manager / Analyst *	PGH-O-015-9

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid/Aqueous
Analytical Method: 8270D
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (8270D)	Check of mass spectral ion intensities (tuning procedure) using DFTPP (8270D)	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method/SOP for specific ion criteria.	Retune instrument and verify.	Lab Manager / Analyst *	PGH-O-001-9
GC/MS (8270D)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit. (ICAL)	Initial calibration prior to sample analysis	Each analyte must meet one of the three options below: Option 1: RSD for each analyte ≤ 15%; Option 2: linear least squares regression for each analyte: r ≥ 0.99; Option 3: 2nd order curves such as quadratic the coefficient of determination (COD) (quadratic) for each analyte: r2 ≥ 0.99.	Evaluate standards, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat initial calibration.	Lab Manager / Analyst *	PGH-O-001-9
			Min. RF requirements presented in Table 8 of the SOP.			PGH-O-001-9

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (8270D)	Initial calibration verification (ICV)	Once after each ICAL	All project analytes within +30% of true value.	Evaluate data. If problem (e.g., concentrated standard, plugged purge line) found, correct, then repeat second source verification. If it still fails, then repeat initial calibration.	Lab Manager / Analyst *	PGH-O-001-9
GC/MS (8270D)	Continuing calibration Standard (CCAL)	Daily, prior to sample analysis and every 12 hours of analysis time.	1. Min RRF for analytes listed in Table 8 ; for analytes not listed in Table 8: RRF > 0.01. 2. %Difference/%Drift for all target compounds and surrogates: %D < 20%	Evaluate standard, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration.	Lab Manager / Analyst *	PGH-O-001-9
GC/MS (8270D)	Internal Standards	During acquisition of calibration standard.	Areas within -50% to +100% of last ICAL mid-point for each CCV ; The retention time shift for each internal standard must be within +/- 30 seconds of its retention time in the most recent continuing calibration standard.	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning	Lab Manager / Analyst *	PGH-O-001-9

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid/Aqueous
Analytical Method: 8270D SIM
Concentration level (if applicable): Low

Instrument	**Calibration Procedure**	**Frequency of Calibration**	**Acceptance Criteria**	**Corrective Action (CA)**	**Person Responsible for CA**	**SOP Reference**
GC/MS (8270D SIM)	Check of mass spectral ion intensities (tuning procedure) using DFTPP (8270D SIM)	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method/SOP for specific ion criteria.	Retune instrument and verify.	Lab Manager / Analyst *	PGH-O-023-5
GC/MS (8270D SIM)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit. (ICAL)	Initial calibration prior to sample analysis	Each analyte must meet one of the three options below: Option 1: RSD for each analyte ≤ 15%; Option 2: linear least squares regression for each analyte: r ≥ 0.99; Option 3: 2nd order curves such as quadratic the coefficient of determination (COD) (quadratic) for each analyte: r2 ≥ 0.99.	Evaluate standards, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat initial calibration.	Lab Manager / Analyst *	PGH-O-023-5

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
			Min. RF requirements presented in Table 5 of the SOP.			PGH-O-023-5
GC/MS (8270D SIM)	Initial calibration verification (ICV)	Once after each ICAL	All project analytes within +30% of true value.	Evaluate data. If problem (e.g., concentrated standard, plugged syringe) found, correct, then repeat second source verification. If it still fails, then repeat initial calibration.	Lab Manager / Analyst *	PGH-O-023-5
GC/MS (8270D SIM)	Continuing calibration Standard (CCV)	Daily, prior to sample analysis and every 12 hours of analysis time.	1. Min RRF for all analytes > 0.05, and meet min. RF in Table 5. 2. %Difference/%Drift for all target compounds and surrogates: %D < 20%	Evaluate standard, chromatography, and mass spectrometer response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration.	Lab Manager / Analyst *	PGH-O-023-5

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (8270D SIM)	Internal Standards	During acquisition of calibration standard.	Areas within -50% to +100% of last ICAL mid-point for each CCV ; The retention time shift for each internal standard must be within +/-30 seconds of its retention time in the most recent continuing calibration standard.	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning	Lab Manager / Analyst *	PGH-O-023-5

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Matrix: Solid/Aqueous
Analytical Method: 8015B (GRO, DRO)
Concentration level (if applicable): Low

Instrument	**Calibration Procedure**	**Frequency of Calibration**	**Acceptance Criteria**	**Corrective Action (CA)**	**Person Responsible for CA**	**SOP Reference**
GC-FID (8015B)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit	Initial calibration prior to sample analysis	RFs determined for Each analyte must meet one of the three options below: Option 1: RSD for each analyte ≤ 20%, or the average of the 5 peaks ≤ 20% ; Option 2: linear least squares regression for each analyte: r ≥ 0.99; Option 3: 2nd order curves such as quadratic the coefficient of determination (COD) (quadratic) for each analyte: r2 ≥ 0.99.	Evaluate standards, chromatography, and detector response. If problem found with above, correct as appropriate,then repeat initial calibration	Lab Manager / Analyst *	WI-PGH-O-003-0 WI-PGH-O-002-0
GC-FID (8015B)	Retention Time Window Position Establishment	Once per ICAL, for each analyte and surrogate.	As outlined in SOP Appendix No. 1	NA	Lab Manager / Analyst *	WI-PGH-O-003-0 WI-PGH-O-002-0

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC-FID (8015B)	Initial calibration verification (ICV)	Immediately following ICAL.	The initial calibration verification standard (ICV from second source) must be within +15% of the initial calibration response.	Evaluate data. If problem (e.g., concentrated standard, plugged injector needle) found, correct, then repeat second source verification. If still fails, repeat initial calibration.	Lab Manager / Analyst *	WI-PGH-O-003-0 WI-PGH-O-002-0
GC-FID (8015B)	Daily calibration verification (CVS)	Beginning of every 12 hour period prior to sample analysis, after every 20 field samples, and at the end of the sequence.	The continuing calibration verification (CCV) standards must have a percent difference that is within +15% of the initial calibration response.	Evaluate standard, chromatography, and detector response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification	Lab Manager / Analyst *	WI-PGH-O-003-0 WI-PGH-O-002-0

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid
Analytical Method: 8082
Concentration level (if applicable): Low

Instrument	**Calibration Procedure**	**Frequency of Calibration**	**Acceptance Criteria**	**Corrective Action (CA)**	**Person Responsible for CA**	**SOP Reference**
GC-ECD (8082)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit	Initial calibration prior to sample analysis	CFs determined for 5 peaks for each aroclor must meet one of the three options below: Option 1: RSD for each analyte ≤ 20%, or the average of the 5 peaks ≤ 20% ; Option 2: linear least squares regression for each analyte: r ≥ 0.99; Option 3: 2nd order curves such as quadratic the coefficient of determination (COD) (quadratic) for each analyte: r2 ≥ 0.99.	Evaluate standards, chromatography, and detector response. If problem found with above, correct as appropriate,then repeat initial calibration	Lab Manager / Analyst *	WI-PGH-O-038-0

Instrument	**Calibration Procedure**	**Frequency of Calibration**	**Acceptance Criteria**	**Corrective Action (CA)**	**Person Responsible for CA**	**SOP Reference**
GC-ECD (8082)	Retention Time Window Position Establishment	Once per ICAL, for each analyte and surrogate.	As outlined in SOP Appendix No. 1	NA	Lab Manager / Analyst *	WI-PGH-O-038-0
GC-ECD (8082)	Initial calibration verification (ICV)	Immediately following ICAL.	All project analytes within ± 20% of the expected value from the ICAL.	Evaluate data. If problem (e.g., concentrated standard, plugged injector needle) found, correct, then repeat second source verification. If still fails, repeat initial calibration.	Lab Manager / Analyst *	WI-PGH-O-038-0

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC-ECD (8082)	Daily calibration verification (CVS)	Beginning of every 12 hour period prior to sample analysis, after every 20 field samples, and at the end of the sequence.	CFs for each aroclor %D $\leq$ 15%.	Evaluate standard, chromatography, and detector response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification	Lab Manager / Analyst *	WI-PGH-O-038-0

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Aqueous
Analytical Method: 680
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (680)	Check of mass spectral ion intensities (tuning procedure) using DFTPP (680)	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method/SOP for specific ion criteria.	Retune instrument and verify.	Lab Manager / Analyst *	S-NY-O-040-rev.08 - PCBs by GCMS - FINAL
GC/MS (680)	WDM	After the tune, and before any initial calibration, and at the beginning of each 12-hour period	Absolute retention times for PCB congeners 77, 104, 189, 202 should not vary by more than $\pm$ 10 seconds from one analysis to the next.	Technical acceptance criteria for the WDM must be met before any standards, samples, QC samples, and required blanks are analyzed. Any analysis conducted when the technical acceptance criteria have not been met will require reanalysis. If the technical acceptance criteria for the WDM are not met, the instrument must be adjusted and the test repeated or the HRGC column must be replaced.	Lab Manager / Analyst *	S-NY-O-040-rev.08 - PCBs by GCMS - FINAL

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (680)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit	Initial calibration prior to sample analysis	RF %RSD must be within 20%. RRF of Internal Standards must meet requirements of Table 2 in the method.	Evaluate standards, chromatography, and detector response. If problem found with above, correct as appropriate, then repeat initial calibration	Lab Manager / Analyst *	S-NY-O-040-rev.08 - PCBs by GCMS - FINAL
GC/MS (680)	Initial calibration verification (ICV)	Immediately following ICAL.	RF %D for all project analytes must be within ± 20% of the mean RF calculated following initial calibration. Internal standard retention times cannot differ by more than 30 sec from those for the initial calibration mid-point standard.	Evaluate data. If problem (e.g., concentrated standard, plugged injector needle) found, correct, then repeat second source verification. If still fails, repeat initial calibration.	Lab Manager / Analyst *	S-NY-O-040-rev.08 - PCBs by GCMS - FINAL

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS (680)	Daily calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the sequence.	%D RR for all project analytes must be within ± 20% of the mean RR calculated following initial calibration. Internal standard retention times cannot differ by more than 30 sec from those for the initial calibration mid-point standard.	Evaluate standard, chromatography, and detector response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification	Lab Manager / Analyst *	S-NY-O-040-rev.08 - PCBs by GCMS - FINAL

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid/Aqueous
Analytical Method: 6010C
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria1	Corrective Action (CA)	Person Responsible for CA	SOP Reference
ICP	Initial calibration (IC) with a minimum of three standards and a calibration blank	Initial calibration prior to sample analysis	Correlation Coefficient ≥ 0.998	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.	Lab Manager / Analyst*	PGH-M-008-16
	Low concentration standard at or near the reporting limit (CRDL/LLCV)	Daily, after one point calibration	Within ± 30% of the true value for all target analytes	Evaluate standard and instrument response. If problem with instrument (autosampler failure, response poor, etc) or standards, correct as appropriate, then repeat. If still fails, repeat initial calibration.	Lab Manager / Analyst*	PGH-M-008-16
	Second-source ICV, prepared at the calibration midpoint	Once per initial calibration	Within ± 10% of the true value for all target analytes.	Evaluate standards and instrument response. If standard issue, repeat or remake then repeat standard as appropriate. If still fails, repeat initial calibration.	Lab Manager / Analyst*	PGH-M-008-16

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria1	Corrective Action (CA)	Person Responsible for CA	SOP Reference
	Continuing calibration verification (CCV), same source as IC	Following IC, after every 10 samples and the end of the sequence	Within ± 10% of the true value for all target analytes.	Evaluate standard and instrument response. If problem with instrument (autosampler failure, response poor, etc) or standards, correct as appropriate, then repeat. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification.	Lab Manager / Analyst*	PGH-M-008-16
	Interference check solution (ICS)	At the beginning of an analytical run	ICSA-A: Absolute values of concentration for all non-spiked analytes <2 X RL (unless they are a verified trace impurity from one of the spiked analytes); ICS-AB: Within ±20% of true value	Terminate analysis, then reanalyze ICS and all affected samples in accordance with method requirements	Lab Manager / Analyst*	PGH-M-008-16

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Matrix: Solid/Aqueous/Air
Analytical Method: 7471B/7470A/NIOSH 6009
Concentration level (if applicable): Low

Instrument	**Calibration Procedure**	**Frequency of Calibration**	**Acceptance Criteria1**	**Corrective Action (CA)**	**Person Responsible for CA**	**SOP Reference**
Cetac Quick Trace Mercury Analyzer M-6100	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit	Daily calibration prior to sample analysis	Linear regression correlation coefficient: r ≥ 0.995	Evaluate standards, and spectrophotometer response. If problem found with above, correct as appropriate,then repeat initial calibration	Lab Manager / Analyst*	PGH-M-017-5 HGVAPOR
	Initial calibration verification (ICV, Second Source)	Immediately following ICAL.	Calculated concentration within ± 10% of the expected value.	Evaluate data. If problem (e.g., concentrated standard, incorrectly prepared standard) found, correct, then repeat second source verification. If still fails, repeat initial calibration.	Lab Manager / Analyst*	PGH-M-017-5 HGVAPOR

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria1	Corrective Action (CA)	Person Responsible for CA	SOP Reference
	Calibration Blank (ICB/CCB)	Immediately following ICV (ICB) and immediately following CCV (CCB).	Result < 1/2 RL.	Evaluate data. If problem found (e.g. contaminated cuvet or solution), correct, then repeat. If still fails, investigate further and repeat initial calibration. Repeat all samples since last successful calibration blank.	Lab Manager / Analyst*	PGH-M-017-5 HGVAPOR
	Continuing calibration verification (CCV)	After every 10 samples, and at the end of the sequence.	Calculated concentration within ± 10% of the expected value.	Evaluate standard and response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification.	Lab Manager / Analyst*	PGH-M-017-5 HGVAPOR

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Matrix: Solid/Aqueous
Analytical Method: 7196A
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria1	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Spectrophoto meter	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit	Daily calibration prior to sample analysis	Linear regression correlation coefficient: r ≥ 0.995	Evaluate standards, and spectrophotometer response. If problem found with above, correct as appropriate,then repeat initial calibration	Lab Manager / Analyst*	PGH-I-012-10
	Initial calibration verification (ICV, Second Source)	Immediately following ICAL.	Calculated concentration within ± 15% of the expected value for aqueous; ± 20% of the expected value for solid.	Evaluate data. If problem (e.g., concentrated standard, incorrectly prepared standard) found, correct, then repeat second source verification. If still fails, repeat initial calibration.	Lab Manager / Analyst*	PGH-I-012-10
	Continuing calibration verification (CCV)	After every 10 field samples, and at the end of the sequence.	Calculated concentration within ± 10% of the expected value.	Evaluate standard and response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification.	Lab Manager / Analyst*	PGH-I-012-10

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid/Aqueous
Analytical Method: 9012A
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria1	Corrective Action (CA)	Person Responsible for CA	SOP Reference
SmartChem and Lachat)	Minimum five-point initial calibration for target analytes, lowest concentration standard at or near the reporting limit	Daily calibration prior to sample analysis	Linear regression correlation coefficient: r ≥ 0.995	Evaluate standards, and spectrophotometer response. If problem found with above, correct as appropriate,then repeat initial calibration	Lab Manager / Analyst*	PGH-I-053-12
	Initial calibration verification (ICV, Two Second Source, Distilled), one high level, one low level	Immediately following ICAL.	Calculated concentrations within ± 10% of the expected value.	Evaluate data. If problem (e.g., concentrated standard, incorrectly prepared standard) found, correct, then repeat second source verification. If still fails, repeat initial calibration.	Lab Manager / Analyst*	PGH-I-053-12
	Continuing calibration verification (CCV)	After every 10 field samples, and at the end of the sequence.	Calculated concentration within ± 10% of the expected value.	Evaluate standard and response. If problem found with above, correct as appropriate, then repeat CCV. If still fails, repeat initial calibration. Re-analyze all samples since the last successful calibration verification.	Lab Manager / Analyst*	PGH-I-053-12

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

Matrix: Solid/Aqueous
Analytical Method: EPA 1664A/ 9071B
Concentration level (if applicable): Low

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria1	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Balance	The calibration of the analytical balance must be verified with 2mg and 1000mg Class S weights prior to and at the conclusion of the mass determinations of the HEM sample analysis. Calibration shall be within ±10% (i.e., ± 0.2 mg) at 2mg and ± 0.5 % (i.e., ± 5 mg) at 1000mg. If values are not within these limits, recalibrate the balance.	Prior to and at the conclusion of the mass determinations of the sample analysis.	Calibration shall be within ±10%	If values are not within these limits, recalibrate the balance. Also make sure that the balance is level.	Lab Manager / Analyst*	PGH-I-042-8, PGH-I-052-7

**The analyst initiates the corrective action and the lab manager and analyst are responsible for the corrective action.*

QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection
(UFP-QAPP Manual Section 3.2.3)
(EPA 2106-G-05 Section 2.3.6)

The laboratory has an established program to maintain instruments and equipment at required levels of calibration and sensitivity, and to minimize loss of productivity due to repairs. Each new piece of equipment is evaluated by senior lab personnel, who also provide technical leadership to solve equipment problems. All equipment and instruments are subjected to routine preventative maintenance, performed primarily by the analysts. Established instructions for maintenance and operation are provided in the areas of the laboratory where the equipment is used. Department managers/supervisors are responsible for inventories of spare parts, including parts with limited durability or availability. Equipment records are maintained for each analytical instrument which include the manufacturer information, first operation date, laboratory location, original condition, operating instructions, calibration details, and any past maintenance or damage. Any equipment with suspected defects is immediately taken out of service until it is repaired and shown to perform satisfactorily. No customer samples are analyzed until reliability has been reestablished. The Pace Analytical Quality Assurance Manual, rev 18, revised 02/08/16 describes procedures for analytical instruments and equipment.

QAPP Worksheet #26 & 27: Sample Handling, Custody, and Disposal
(UFP-QAPP Manual Section 3.3)
(EPA 2106-G-05 Section 2.3.3)

Sampling Organization: EAG/ARM/KEY/ARC

Laboratory: PACE

Method of sample delivery (shipper/carrier): Field Personnel - FedEx – Pace Courier

Number of days from reporting until sample disposal: Per laboratory SOPs – see worksheet 19 & 30

Activity	Organization and title or position of person responsible for the activity	SOP reference
Sample labeling	Task Manager	SOP 011
Chain-of-custody form completion	Task Manager	
Packaging	Task Manager	
Shipping coordination	Project Manager	
Sample receipt, inspection, & log-in	PACE	Consult Laboratory SOPs referenced on Worksheets 19 & 30
Sample custody and storage	PACE	Consult Laboratory SOPs referenced on Worksheets 19 & 30
Sample disposal	PACE	Consult Laboratory SOPs referenced on Worksheets 19 & 30

QAPP Worksheet #28: Analytical Quality Control and Corrective Action
(UFP-QAPP Manual Section 3.4)
(EPA 2106-G-05 Section 2.3.5)

Matrix: Soil Vapor
Analytical Group: Volatiles
Analytical Method/SOP: TO-15/ S-LI-O-022-rev.01

TABLE 28-1: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Check of mass spectral ion intensities (tuning procedure) using BFB (TO- 15)	Prior to initial calibration and calibration verification	Must meet the method requirements before samples are analyzed in accordance with EPA Method requirements	Retune instrument and verify the tune acceptability in accordance with EPA Method requirements	Lab Manager / Analyst	Sensitivity	Must meet the method requirements before samples are analyzed
Internal standards	During acquisition of calibration standard, samples, and QC check samples	Areas within 60% to 140% of midpoint of the last ICAL for each sample and QC; RT < 0.33 min daily std.	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning in accordance with EPA Method requirements	Lab Manager / Analyst	Precisions and Accuracy/Bias	Areas within 60% to 140% of midpoint of the last ICAL for each sample and QC; RT < 0.33 min daily std.
Method blank	One per analytical batch (20 samples) (TO-15)	No target analytes ≥ RL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with EPA Method requirements.	Lab Manager / Analyst	Accuracy/Bias Contamination	No target analytes ≥ RL

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Duplicate	One Duplicate per analytical/preparation batch (20 samples)	%RPD $\leq$ 25%	Note in Case Narrative	Lab Manager / Analyst	Precision and Accuracy/Bias	%RPD $\leq$ 25%
LFB	One LFB per analytical/preparation batch (20 samples)	70-130%	Reanalyze. If a re-analysis of a LFB is still noncompliant, The standards preparation and equipment must be evaluated, Prepare new standards. Reanalyze all samples.	Lab Manager / Analyst	Precision and Accuracy/Bias	70-130%
Surrogate standards	All field and QC samples.	70-130%	If % recoveries are outside the range, reanalysis is required, unless no positives are found and surrogate recovery was high. If the sample reanalysis also fails the recovery criteria, report all data for the sample as "suspect".	Lab Manager / Analyst	Accuracy/Bias	70-130%

Table 28-2: Recovery & Precision Limits (Soil Vapor)

Analyte	Precision (RPD)	Recovery Limits (LCS)
1,1,1-Trichloroethane	25	70-130%
1,1,2,2-Tetrachloroethane	25	70-130%
1,1,2-Trichloroethane	25	70-130%
1,1-Dichloroethane	25	70-130%
1,1-Dichloroethene	25	70-130%
1,2,4-Trichlorobenzene	25	70-130%
1,2,4-Trimethylbenzene	25	70-130%
4-Ethyltoluene	25	70-130%
1,3-Butadiene	25	70-130%
1,2-Dibromoethane (EDB)	25	70-130%
1,2-Dichlorobenzene	25	70-130%
1,2-Dichloroethane	25	70-130%
1,2-Dichloropropane	25	70-130%
1,3,5-Trimethylbenzene	25	70-130%
1,3-Dichlorobenzene	25	70-130%
1,3-Dichloropropane	25	70-130%
1,4-Dichlorobenzene	25	70-130%
2-Butanone (MEK)	25	70-130%
alpha-Chlorotoluene	25	70-130%
2-Hexanone	25	70-130%
1,4-Dioxane	25	70-130%
4-Methyl-2-pentanone (MIBK)	25	70-130%
Acetone	25	70-130%
Benzene	25	70-130%
Bromodichloromethane	25	70-130%
Bromoform	25	70-130%
Bromomethane	25	70-130%
Carbon disulfide	25	70-130%
Carbon tetrachloride	25	70-130%
Chlorobenzene	25	70-130%
Chloroethane	25	70-130%
Chloroform	25	70-130%
Chloromethane	25	70-130%
cis-1,2-Dichloroethene	25	70-130%
cis-1,3-Dichloropropene	25	70-130%
Cyclohexane	25	70-130%
Dibromochloromethane	25	70-130%
Freon 11 (Trichlorofluoromethane)	25	70-130%
Dichlorodifluoromethane (Freon 12)	25	70-130%
Freon 113 (Trichlorotrifluoromethane)	25	70-130%
Freon 114	25	70-130%
Ethylbenzene	25	70-130%

Analyte	Precision (RPD)	Recovery Limits (LCS)
Heptane	25	70-130%
Hexachlorobutadiene	25	70-130%
Hexane	25	70-130%
Isopropylbenzene	25	70-130%
Methyl tert-butyl ether (MTBE)	25	70-130%
Methylene chloride	25	70-130%
m,p-Xylene	25	70-130%
Naphthalene	25	70-130%
Propylene	25	70-130%
n-Propylbenzene	25	70-130%
o-Xylene	25	70-130%
Ethanol	25	70-130%
2-Propanol	25	70-130%
Styrene	25	70-130%
Tetrahydrofuran	25	70-130%
Tetrachloroethene	25	70-130%
Toluene	25	70-130%
trans-1,2-Dichloroethene	25	70-130%
trans-1,3-Dichloropropene	25	70-130%
Trichloroethene	25	70-130%
Vinyl Acetate	25	70-130%
Vinyl chloride	25	70-130%
1,4-Dioxane	25	70-130%
1,2-Dibromomethane	25	70-130%
1,2-Dibromo-3-chloropropane	NA	NA
1,2,3-Trichlorobenzene	NA	NA
1,2,4-Trichlorobenzene	25	70-130%
1,2-Dichlorobenzene	25	70-130%
1,4-Dichlorobenzene	25	70-130%
1,2-Dichloroethane-d4	NA	70-130%
Toluene-d8 (Surrogate)	NA	70-130%
4-Bromofluorobenzene	NA	70-130%

Matrix: Soil/Aqueous
Analytical Group: Volatiles
Analytical Method/SOP: 8260B/ PGH-O-015-9

TABLE 28-3: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Check of mass spectral ion intensities (tuning procedure) using BFB (8260B)	Prior to initial calibration and calibration verification	Must meet the method requirements before samples are analyzed in accordance with EPA method requirements	Retune instrument and verify the tune acceptability in accordance with EPA Method requirements	Lab Manager / Analyst	Sensitivity	Must meet the method requirements before samples are analyzed in accordance with EPA method requirements
Internal standards	During acquisition of calibration standard, samples, and QC check samples	Areas within -50% to +100% of midpoint of the last ICAL for each sample and QC in accordance with EPA method requirements	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning in accordance with EPA Method requirements	Lab Manager / Analyst	Precision and Accuracy/Bias	Areas within -50% to +100% of midpoint of the last ICAL for each sample and QC in accordance with EPA method requirements

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per analytical batch (20 samples) (8260B)	No target compounds >RL except common lab contaminants which should be <2xRL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements.	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL except common lab contaminants which should be <2xRL
MS/MSD	One MS/MSD per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-4 and Table 28-5	If LCS results are acceptable then MS/MSD are attributed to matrix interference. Results must be evaluated and documented.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-4 and Table 28-5

LCS	One LCS per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-4 and Table 28-5	An out-of-control LCS must be reanalyzed along with associated samples.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-4 and Table 28-5
QC Sample	**Frequency / Number**	**Method / SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Surrogate standards	All field and QC samples.	Table 28-4 and Table 28-5	Evaluate matrix, then analytical data, then reanalyze all affected samples in accordance with EPA Method requirements as appropriate. Qualify outliers.	Lab Manager / Analyst	Accuracy/Bias	Acceptance criteria are specified in Table 28-4 and Table 28-5

Table 28-4A: MS/MSD Recovery & Precision Limits (Soil)

Matrix: Solid

Analytical Group: Volatiles

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
1,1,1,2-Tetrachloroethane	30	10 - 146
1,1,1-Trichloroethane	30	13 - 144
1,1,2,2-Tetrachloroethane	30	10 - 145
1,1,2-Trichloroethane	30	10 - 143
1,1-Dichloroethane	30	28 - 130
1,1-Dichloroethene	30	11 - 151
1,1-Dichloropropene	30	22 - 144
1,2,3-Trichlorobenzene	30	10 - 134
1,2,3-Trichloropropane	30	13 - 171
1,2,4-Trichlorobenzene	30	10 - 130
1,2,4-Trimethylbenzene	30	10-150
1,2-Dibromo-3-chloropropane (DBCP)	30	10-148
1,2-Dibromoethane (EDB)	30	10-139
1,2-Dichlorobenzene	30	10-125
1,2-Dichloroethane	30	21-127
1,2-Dichloropropane	30	21-132
1,3,5-Trimethylbenzene	30	10-155
1,3-Dichlorobenzene	30	10-127
1,3-Dichloropropane	30	15-155
1,4-Dichlorobenzene	30	10-127
2,2-Dichloropropane	30	23-145
2-Butanone (MEK)	30	10-175
2-Chlorotoluene	30	10-140
2-Hexanone	30	10-175
4-Chlorotoluene	30	10-137
4-Methyl-2-pentanone (MIBK)	30	10-167
Acetone	30	10-175
Benzene	30	10-151
Bromobenzene	30	10-144
Bromochloromethane	30	35-117
Bromodichloromethane	30	10-124
Bromoform	30	10-124
Bromomethane	30	10-163
Carbon disulfide	30	10-185

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
Carbon tetrachloride	30	10-146
Chlorobenzene	30	10-131
Chloroethane	30	19-162
Chloroform	30	28-124
Chloromethane	30	10-166
cis-1,2-Dichloroethene	30	20-126
cis-1,3-Dichloropropene	30	10-123
Dibromochloromethane	30	10-133
Dibromomethane	30	25-141
Ethylbenzene	30	10-157
Hexachlorobutadiene	30	10-135
Isopropylbenzene	30	10-146
Methyl tert-butyl ether (MTBE)	30	35-155
Methylene chloride	30	10-130
m-Xylene & p-Xylene	30	10-150
n-Butylbenzene	30	10-141
n-Propylbenzene	30	10-141
o-Xylene	30	10-152
p-Isopropyltoluene	30	10-142
sec-Butylbenzene	30	10-150
Styrene	30	10-134
tert-Butylbenzene	30	10-148
Tetrachloroethene	30	10-155
Toluene	30	10-139
trans-1,2-Dichloroethene	30	16-131
trans-1,3-Dichloropropene	30	10-125
Trichloroethene	30	10-153
Vinyl chloride	30	21-147
Dichlorodifluoromethane	30	10-175
Trichlorofluoromethane	30	10-169
1,1,2-Trichloro-1,2,2-trifluoroethane	30	10-175
Methyl Acetate	30	10-175
Cyclohexane	30	24-139
2-Hexanone	30	10-175
1,2-Dichlorobenzene	30	10-125
1,3-Dichlorobenzene	30	10-127
1,4-Dichlorobenzene	30	10-127
1,2,3-Trichlorobenzene	30	10-134

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
1,2,4-Trichlorobenzene	30	10-130
1,4-Dioxane	30	25-188
1,2-Dichloroethane-d4 (Surrogate)	--	69-137
4-Bromofluorobenzene (Surrogate)	--	65-146
Dibromofluoromethane (Surrogate)	--	70-130
Toluene-d8 (Surrogate)	--	68-135

Table 28-4B: MS/MSD Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
1,1,1,2-Tetrachloroethane	30	52-120
1,1,1-Trichloroethane	30	54-140
1,1,2,2-Tetrachloroethane	30	54-124
1,1,2-Trichloroethane	30	58-120
1,1-Dichloroethane	30	55-133
1,1-Dichloroethene	30	48-141
1,1-Dichloropropene	30	56-140
1,2,3-Trichlorobenzene	30	40-123
1,2,3-Trichloropropane	30	51-116
1,2,4-Trichlorobenzene	30	33-130
1,2,4-Trimethylbenzene	30	69-121
1,2-Dibromo-3-chloropropane (DBCP)	30	23-126
1,2-Dibromoethane (EDB)	30	58-115
1,2-Dichlorobenzene	30	57-124
1,2-Dichloroethane	30	58-123
1,2-Dichloropropane	30	55-125
1,3,5-Trimethylbenzene	30	68-118
1,3-Dichlorobenzene	30	62-113
1,3-Dichloropropane	30	59-120
1,4-Dichlorobenzene	30	61-111
2,2-Dichloropropane	30	32-137
2-Butanone (MEK)	30	43-128
2-Chlorotoluene	30	58-114
2-Hexanone	30	43-135
4-Chlorotoluene	30	58-113
4-Methyl-2-pentanone (MIBK)	30	47-123
Acetone	30	10-150
Benzene	30	63-123
Bromobenzene	30	57-116
Bromochloromethane	30	42-149
Bromodichloromethane	30	55-127
Bromoform	30	44-131
Bromomethane	30	10-149
Carbon disulfide	30	47-158

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
Carbon tetrachloride	30	44-155
Chlorobenzene	30	57-121
Chloroethane	30	57-156
Chloroform	30	56-132
Chloromethane	30	42-163
cis-1,2-Dichloroethene	30	46-139
cis-1,3-Dichloropropene	30	55-119
Dibromochloromethane	30	52-129
Dibromomethane	30	52-120
Dichlorodifluoromethane (Freon 12)	30	10-175
Ethylbenzene	30	70-120
Hexachlorobutadiene	30	29-131
Isopropylbenzene	30	71-129
Methyl tert-butyl ether (MTBE)	30	63-143
Methylene chloride	30	38-134
m-Xylene & p-Xylene	30	70-123
n-Butylbenzene	30	52-123
n-Propylbenzene	30	59-123
o-Xylene	30	68-122
p-Isopropyltoluene	30	56-125
sec-Butylbenzene	30	57-124
Styrene	30	49-135
tert-Butylbenzene	30	59-121
Tetrachloroethene	30	53-125
Toluene	30	66-124
trans-1,2-Dichloroethene	30	52-136
trans-1,3-Dichloropropene	30	54-118
Trichloroethene	30	50-127
Trichlorofluoromethane (Freon 11)	30	63-167
Vinyl chloride	30	54-149
Dichlorodifluoromethane	30	10-175
Trichlorofluoromethane	30	63-137
1,1,2-Trichloro-1,2,2-trifluoroethane	30	41-186
Methyl Acetate	30	25-127
Cyclohexane	30	10-143
2-Hexanone	30	43-135

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
1,2-Dichlorobenzene	30	57-124
1,3-Dichlorobenzene	30	62-113
1,4-Dichlorobenzene	30	61-111
1,2,3-Trichlorobenzene	30	40-123
1,2,4-Trichlorobenzene	30	33-130
1,2-Dichloroethane-d4 (Surrogate)	--	77-126
4-Bromofluorobenzene (Surrogate)	--	81-119
Dibromofluoromethane (Surrogate)	--	70-130
Toluene-d8 (Surrogate)	--	84-115

Table 28-5A: LCS Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (LCS)
1,1,1,2-Tetrachloroethane	20	64 - 124
1,1,1-Trichloroethane	20	67 - 129
1,1,2,2-Tetrachloroethane	20	58 - 128
1,1,2-Trichloroethane	20	69 -120
1,1,2-Trichlorotrifluoroethane	20	48 - 171
1,1-Dichloroethane	20	66 -129
1,1-Dichloroethene	20	59 - 133
1,1-Dichloropropene	20	66 - 124
1,2,3-Trichlorobenzene	20	50 - 156
1,2,3-Trichloropropane	20	68 - 118
1,2,4-Trichlorobenzene	20	32 - 159
1,2,4-Trimethylbenzene	20	75 - 128
1,2-Dibromo-3-chloropropane	20	41 - 136
1,2-Dibromoethane (EDB)	20	66 - 124
1,2-Dichlorobenzene	20	67 - 128
1,2-Dichloroethane	20	66 - 123
1,2-Dichloropropane	20	69 -121
1,3,5-Trimethylbenzene	20	74 - 125
1,3-Dichlorobenzene	20	68 - 121
1,3-Dichloropropane	20	73 - 119
1,4-Dichlorobenzene	20	70 - 117
1,4-Dioxane	20	18 - 175
2,2-Dichloropropane	20	25 - 144
2-Butanone (MEK)	20	57 - 126
2-Chloroethylvinyl ether	20	10 - 160
2-Chlorotoluene	20	69 - 119
2-Hexanone	20	57 - 129
2-Methylnaphthalene	20	30 - 175
4-Chlorotoluene	20	70 - 118
4-Methyl-2-pentanone (MIBK)	20	65 - 119
Acetone	20	35 - 113
Acetonitrile	20	45 - 158
Acrylonitrile	20	35 - 187
Allyl Chloride	20	47 - 173
Benzene	20	69 - 115
Bromobenzene	20	66 - 122
Bromochloromethane	20	62 - 125
Bromodichloromethane	20	69 - 132
Bromoform	20	52 - 142
Bromomethane	20	14 - 151
Carbon Disulfide	20	53 - 156

Table 28-5A: LCS Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (LCS)
Carbon Tetrachloride	20	65 - 138
Chlorobenzene	20	69 - 120
Chloroethane	20	62- 134
Chloroform	20	67 -123
Chloromethane	20	54 -143
cis-1,2-Dichloroethene	20	66 -122
cis-1,3-Dichloropropene	20	64 - 125
Cyclohexane	20	36 - 165
Cyclohexanone	20	31 -114
Dibromochloromethane	20	61 - 135
Dibromomethane	20	61 - 131
Dichlorodifluoromethane	20	26 - 173
Diethyl ether (Ethyl Ether)	20	54 - 148
Diisopropyl Ether	20	60 - 131
Ethanol	20	10 - 175
Ethyl methacrylate	20	24 - 129
Ethylbenzene	20	71 - 116
Ethyl-tert-butyl-ether	20	64 - 141
Hexachloro-1,3-Butadiene	20	44 - 155
Iodomethane	20	10 - 166
Isobutanol	20	31 - 172
Isopropylbenzene (Cumene)	20	79 - 121
m,p-Xylene	20	74 - 118
Methacrylonitrile	20	56 - 126
Methyl Acetate	20	41 - 155
Methyl methacrylate	20	48 - 155
Methylcyclohexane	20	51 - 152
Methylene Chloride	20	56 - 130
Methyl-tert-butyl-ether (MTBE)	20	83 - 140
Naphthalene	20	64 - 140
n-Butylbenzene	20	64 - 128
n-Hexane	20	28 - 154
n-Propylbenzene	20	70 - 123
o-Xylene	20	71 - 119
p-Isopropyltoluene	20	68 - 129
Propionitrile	20	65 - 125
sec-Butylbenzene	20	70 - 126
Styrene	20	71 - 129
tert-Amylmethyl ether	20	61 - 115
tert-Butyl Alcohol (TBA)	20	32 - 161
tert-Butyl Benzne	20	72 - 123

Table 28-5A: LCS Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (LCS)
Tetrachloroethene	20	62 - 122
Tetrahydrofuran	20	53 - 132
Toluene	20	70 - 115
Total Xylenes	20	73 - 118
trans-1,2-Dichloroethene	20	63 - 130
trans-1,3-Dichloropropene	20	62 - 122
trans-1,4-Dichloro-2-butene	20	28 - 120
Trichloroethene	20	61 - 126
Trichlorofluoromethane	20	64 - 133
Vinyl acetate	20	10 - 62
Vinyl chloride	20	58 - 127
1,2-Dichloroethane-d4 (S)	20	77 - 126
4-Bromofluorobenzene (S)	20	81 - 119
Toluene-d8 (S)	20	84 - 115
Dibromofluoromethane (S)	20	70 - 130

Table 28-5B: LCS Recovery & Precision Limits (Solid)

Analyte	Precision (RPD)	Recovery Limits (LCS)
1,1,1,2-Tetrachloroethane	25	59 - 126
1,1,1-Trichloroethane	25	71 - 130
1,1,2,2-Tetrachloroethane	25	66 - 123
1,1,2-Trichloroethane	25	75 - 115
1,1,2-Trichlorotrifluoroethane	25	21 -175
1,1-Dichloroethane	25	65 - 126
1,1-Dichloroethene	25	62 - 137
1,1-Dichloropropene	25	50 - 144
1,2,3-Trichlorobenzene	25	65 - 135
1,2,3-Trichloropropane	25	63 - 120
1,2,4-Trichlorobenzene	25	78 - 137
1,2,4-Trimethylbenzene	25	79 - 125
1,2-Dibromo-3-chloropropane	25	21 - 150
1,2-Dibromoethane (EDB)	25	74 - 118
1,2-Dichlorobenzene	25	82 - 121
1,2-Dichloroethane	25	67 - 116
1,2-Dichloropropane	25	67 - 119
1,3,5-Trimethylbenzene	25	74 - 129
1,3-Dichlorobenzene	25	80 - 124
1,3-Dichloropropane	25	65 - 121
1,4-Dichlorobenzene	25	80 - 126
1,4-Dioxane	25	40 - 132
2,2-Dichloropropane	25	32 - 155
2-Butanone (MEK)	25	42 - 116
2-Chloroethylvinyl ether	25	16 - 145
2-Chlorotoluene	25	62 - 131
2-Hexanone	25	54 - 121
2-Methylnaphthalene	25	44 - 151
4-Chlorotoluene	25	58 - 131
4-Methyl-2-pentanone (MIBK)	25	52 - 119
Acetone	25	32 - 113
Acetonitrile	25	29 - 144
Acrylonitrile	25	37 - 137
Allyl Chloride	25	40 - 166
Benzene	25	71 - 137
Bromobenzene	25	52 - 135
Bromochloromethane	25	63 - 127
Bromodichloromethane	25	67 - 121
Bromoform	25	58 - 122
Bromomethane	25	27 - 164
Carbon Disulfide	25	60 - 172

Table 28-5B: LCS Recovery & Precision Limits (Solid)

Analyte	Precision (RPD)	Recovery Limits (LCS)
Carbon Tetrachloride	25	66 - 132
Chlorobenzene	25	80 - 119
Chloroethane	25	53 - 149
Chloroform	25	70 - 120
Chloromethane	25	47 - 147
cis-1,2-Dichloroethene	25	64 - 120
cis-1,3-Dichloropropene	25	67 - 123
Cyclohexane	25	45 - 190
Cyclohexanone	25	10 - 120
Dibromochloromethane	25	67 - 120
Dibromomethane	25	54 - 123
Dichlorodifluoromethane	25	10 - 175
Diethyl ether (Ethyl Ether)	25	57 - 124
Diisopropyl Ether	25	47 - 126
Ethanol	25	23 - 168
Ethyl Acetate	25	10 - 169
Ethyl methacrylate	25	10 - 125
Ethylbenzene	25	78 - 126
Ethyl-tert-butyl-ether	25	49 - 122
Hexachloro-1,3-Butadiene	25	52 - 156
Iodomethane	25	28 - 144
Isobutanol	25	24 - 137
Isopropylbenzene (Cumene)	25	78 - 133
m,p-Xylene	25	77 - 129
Methacrylonitrile	25	41 - 118
Methyl Acetate	25	50 - 130
Methyl methacrylate	25	23 - 167
Methylcyclohexane	25	31 - 175
Methylene Chloride	25	50 - 125
Methyl-tert-butyl-ether (MTBE)	25	77 - 141
Naphthalene	25	81 - 126
n-Butylbenzene	25	74 - 140
n-Hexane	25	10 - 175
n-Propylbenzene	25	70 - 140
o-Xylene	25	80 - 125
p-Isopropyltoluene	25	74 - 136
Propionitrile	25	64 - 121
sec-Butylbenzene	25	81 - 132
Styrene	25	79 - 130
tert-Amylmethyl ether	25	50 - 117
tert-Butyl Alcohol (TBA)	25	45 - 134

Table 28-5B: LCS Recovery & Precision Limits (Solid)

Analyte	Precision (RPD)	Recovery Limits (LCS)
tert-Butyl Benzne	25	77 - 129
Tetrachloroethene	25	73 - 135
Tetrahydrofuran	25	31 - 138
Toluene	25	72 - 127
Total Xylenes	25	80 - 124
trans-1,2-Dichloroethene	25	64 - 131
trans-1,3-Dichloropropene	25	66 - 116
trans-1,4-Dichloro-2-butene	25	25 - 117
Trichloroethene	25	73 - 125
Trichlorofluoromethane	25	39 - 192
Vinyl acetate	25	23 - 26
Vinyl chloride	25	46 - 138
1,2-Dichloroethane-d4 (S)	25	69 - 137
4-Bromofluorobenzene (S)	25	65 - 146
Toluene-d8 (S)	25	68 - 135
Dibromofluoromethane (S)	25	70 - 130

Analytical Group: Semivolatiles
Analytical Method/8270D/SOP: PGH-O-001-8

TABLE 28-6: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Check of mass spectral ion intensities (tuning procedure) using DFTPP (8270D)	Prior to initial calibration and calibration verification	Must meet the method requirements before samples are analyzed in accordance with EPA method requirements	Retune instrument and verify the tune acceptability in accordance with EPA Method requirements	Lab Manager / Analyst	Sensitivity	Must meet the method requirements before samples are analyzed in accordance with EPA method requirements
Internal standards	During acquisition of calibration standard, samples, and QC check samples	Areas within -50% to +100% of midpoint of the last ICAL for each sample and QC in accordance with EPA method requirements	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning in accordance with EPA Method requirements	Lab Manager / Analyst	Precision and Accuracy/Bias	Areas within -50% to +100% of midpoint of the last ICAL for each sample and QC in accordance with EPA method requirements

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per analytical batch (20 samples) (8270D)	No target compounds >RL except common lab contaminants which should be <2xRL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements.	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL except common lab contaminants which should be <2xRL
MS/MSD	One MS/MSD per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-7 and Table 28-8	If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-7 and Table 28-8

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
LCS	One LCS per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-7 and Table 28-8	Correct problem and, then re-extract and reanalyze all affected samples in accordance with Method/SOP requirements as appropriate.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-7 and Table 28-8
Surrogate standards	All field and QC samples.	Acceptance criteria are specified in Table 28-7 and Table 28-8	Correct problem and, then re-extract and reanalyze all affected samples in accordance with Method/SOP requirements as appropriate.	Lab Manager / Analyst	Accuracy/Bias	Acceptance criteria are specified in Table 28-7 and Table 28-8

Table 28-7: Recovery & Precision Limits (Soil)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
1,2,4-Trichlorobenzene	25	35 - 65
1,2-Dichlorobenzene	25	37 - 77
1,3-Dichlorobenzene	25	35 - 74
1,4-Dichlorobenzene	25	39 - 77
1-Methylnaphthalene	25	38 - 70
2,4,5-Trichlorophenol	25	47 - 88
2.4.6-Trichlorophenol	25	44 - 86
2.4-Dichlorophenol	25	36 - 65
2,4-Dimethylphenol	25	34 - 60
2,4-Dinitrophenol	25	33 - 76
2,4-Dinitrotoluene	25	68 - 92
2,6-Dinitrotoluene	25	53 - 96
2-Chloronaphthalene	25	40 - 86
2-Chlorophenol	25	36 - 74
2-Methylnaphthalene	25	34 - 60
2-Methylphenol (o-cresol)	25	38 - 74
2-Nitroaniline	25	52 - 93
2-Nitrophenol	25	30 - 65
3,4-Methylphenol (mp- cresol)	25	40 - 77
3-Nitroaniline	25	62 - 85
4,6-Dinitro-2-methylphenol	25	68 - 92
4-Bromophenylphenyl ether	25	52 - 93
4-Chloro-3-Methylphenol	25	40 - 71
4-Chloroaniline	25	30 - 53
4-Chlorophenylphenyl ether	25	46 - 89
4-Nitroaniline	25	67 - 94
4-Nitrophenol	25	72 - 93
Acenaphthene	25	44 - 86
Acenaphthylene	25	42 - 85
Anthracene	25	65 - 90
Benzo(a)anthracene	25	75 - 96
Benzo(a)pyrene	25	76 - 94
Benzo(b)fluoranthene	25	72 - 101
Benzo(g,h,i)pyrelene	25	10 - 117
Benzo(k)fluoranthene	25	78 - 108
Benzyl Alcohol	25	39 - 80
Benzoic Acid	25	10 - 44
Butylbenzyl phthalate	25	77 - 103
Carbazole	25	74 - 100
Chrysene	25	77 - 97

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
Di-n-butyl phthalate	25	77 - 97
Di-n-octyl phthalate	25	79 - 97
Dibenz(a,h)anthracene	25	17 - 112
Diethylphthalate	25	57 - 91
Dimethylphthalate	25	54 - 91
Fluoranthene	25	68 - 92
Fluorene	25	48 - 88
Hexachloro-1,3-butadiene	25	35 - 64
Hexachlorobenzene	25	58 - 95
Hexachlorocyclopentadiene	25	28 - 64
Hexachloroethane	25	36 - 76
Indeno(1,23-cd)pyrene	25	22 - 114
Isophorone	25	36 - 67
N-Nitroso-di-n-propylamine	25	38 - 81
N-Nitrosodimethylamine	25	34 - 78
N-Nitrosodiphenylamine	25	48 - 71
Naphthalene	25	36 - 63
Nitrobenzene	25	35 - 64
Pentachlorophenol	25	57 - 73
Phenanthrene	25	66 - 90
Phenol	25	37 - 73
Pyrene	25	77 - 102
bis(2- chloroethoxy)methane	25	33 - 64
bis(2-chloroethyl)ether	25	36 - 75
bis(2-chloroisopropyl)ether	25	33 - 69
bis(2-Ethylhexyl) phthalate	25	76-102
Acetophenone	25	38 - 76
Benzaldehyde	25	10 - 175
1,1'-Biphenyl	25	40 - 82
Bis(2-Chloroethoxy) methane	25	33 - 64
Caprolactum	25	58 - 77
3,3'-Dichlorobenzidine	25	58 - 75
Di-n-octylphthalate	25	79 - 97
2-Nitroaniline	25	52 - 93
4-Nitroaniline	25	67 - 94
1,2,4,5-tetrachlorobenzene	25	39 - 78
2,3,4,6-tetrachlorophenol	25	57 - 79
Nitrobenzene-d5 (Base/Neutral)	NA	33 - 59
2-Fluorobiphenyl (Base/Neutral)	NA	37 - 76
Terphenyl-d14	NA	67 - 94
Phenol-d5 (Acid)	NA	35 - 72
2-Fluorophenol	NA	30 - 67
2,4,6-Tribromophenol (Acid)	NA	53 - 83

Table 28-8: Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
1,2,4-Trichlorobenzene	25	37-99
1,2-Dichlorobenzene	25	31-112
1,3-Dichlorobenzene	25	29-108
1,4-Dichlorobenzene	25	34-91
1-Methylnaphthalene	25	46-107
2,4,5-Trichlorophenol	25	23-160
2.4.6-Trichlorophenol	25	51-127
2.4-Dichlorophenol	25	32-126
2,4-Dimethylphenol	25	30-124
2,4-Dinitrophenol	25	10-170
2,4-Dinitrotoluene	25	46-107
2,6-Dinitrotoluene	25	14-167
2-Chloronaphthalene	25	42-114
2-Chlorophenol	25	40-100
2-Methylnaphthalene	25	43-100
2-Methylphenol (o-cresol)	25	32-116
2-Nitroaniline	25	35-144
2-Nitrophenol	25	29-129
3,4-Methylphenol (mp- cresol)	25	30-103
3-Nitroaniline	25	20-163
4,6-Dinitro-2-methylphenol	25	20-154
4-Bromophenylphenyl ether	25	41-133

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
4-Chloro-3-Methylphenol	25	40-111
4-Chloroaniline	25	10-148
4-Chlorophenylphenyl ether	25	25-154
4-Nitroaniline	25	42-157
4-Nitrophenol	25	10-57
Acenaphthene	25	45-105
Acenaphthylene	25	45-106
Anthracene	25	54-107
Benzo(a)anthracene	25	68-106
Benzo(a)pyrene	25	60-108
Benzo(b)fluoranthene	25	63-120
Benzo(g,h,i)pyrelene	25	29-139
Benzo(k)fluoranthene	25	64-122
Benzyl Alcohol	25	16-121
Benzoic Acid	25	10-80
Butylbenzyl phthalate	25	40-153
Carbazole	25	51-142
Chrysene	25	69-103
Di-n-butyl phthalate	25	24-159
Di-n-octyl phthalate	25	40-148
Dibenz(a,h)anthracene	25	39-132
Diethylphthalate	25	52-127
Dimethylphthalate	25	52-128
Fluoranthene	25	64-114

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
Fluorene	25	49-110
Hexachloro-1,3-butadiene	25	36-117
Hexachlorobenzene	25	53-128
Hexachlorocyclopentadiene	25	20-88
Hexachloroethane	25	26-110
Indeno(1,23-cd)pyrene	25	37-131
Isopherone	25	30-123
N-Nitroso-di-n-propylamine	25	41-110
N-Nitrosodimethylamine	25	13-90
N-Nitrosodiphenylamine	25	43-134
Naphthalene	25	45-101
Nitrobenzene	25	26-130
Pentachlorophenol	25	28-131
Phenanthrene	25	59-109
Phenol	25	15-46
Pyrene	25	53-115
bis(2- chloroethoxy)methane	25	36-129
bis(2-chloroethyl)ether	25	31-123
bis(2-chloroisopropyl)ether	25	28-124
bis(2-Ethylhexyl) phthalate	25	30-177
Acetophenone	25	10 - 175
Benzaldehyde	25	10 - 175
1,1'-Biphenyl	25	10 - 175
Bis(2-Chloroethoxy) methane	25	36-129

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
Caprolactum	25	10 - 175
3,3'-Dichlorobenzidine	25	32 - 196
Di-n-octylphthalate	25	–40-148
2-Nitroaniline	25	35-144
4-Nitroaniline	25	42-157
1,2,4,5-tetrachlorobenzene	25	10 - 175
2,3,4,6-tetrachlorophenol	25	10 - 175
Nitrobenzene-d5 (Base/Neutral)	NA	22-128
2-Fluorobiphenyl (Base/Neutral)	NA	34-113
Terphenyl-d14	NA	35-150
Phenol-d5 (Acid)	NA	14-49
2-Fluorophenol	NA	19-70
2,4,6-Tribromophenol (Acid)	NA	34-134

Analytical Group: Semivolatiles
Analytical Method/8270D SIM/SOP: PGH-O-023-5

TABLE 28-9: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Check of mass spectral ion intensities (tuning procedure) using DFTPP (8270D-SIM)	Prior to initial calibration and calibration verification	Must meet the method requirements before samples are analyzed in accordance with EPA method requirements	Retune instrument and verify the tune acceptability in accordance with EPA Method requirements	Lab Manager / Analyst	Sensitivity	Must meet the method requirements before samples are analyzed in accordance with EPA method requirements
Internal standards	During acquisition of calibration standard, samples, and QC check samples	Areas within -50% to +100% of midpoint of the last ICAL for each sample and QC in accordance with EPA method requirements Retention time within 30 seconds of ICAL mid-point	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning in accordance with EPA Method requirements.	Lab Manager / Analyst	Precision and Accuracy/Bias	Areas within -50% to +100% of midpoint of the last ICAL for each sample and QC in accordance with EPA method requirements Retention time within 30 seconds of ICAL mid-point

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per analytical batch (20 samples) (8270D-SIM)	No target compounds >RL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements.	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL
MS/MSD	One MS/MSD per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-10 and Table 28-111	Identify problem; if not related to matrix interference, re-extract and reanalyze MS/MSD in accordance with method/SOP requirements	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-10 and Table 28-111

LCS	One LCS per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-10 and Table 28-111	Reanalyze LCS once. If acceptable, report. Otherwise, evaluate and reprep and reanalyze the LCS and all samples in the associated prep batch for failed analytes, if sufficient sample material is available.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-10 and Table 28-111
QC Sample	**Frequency / Number**	**Method / SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Surrogate standards	All field and QC samples.	Acceptance criteria are specified in Table 28-10 and Table 28-111	Evaluate matrix, then analytical data, then re-extract and reanalyze all affected samples in accordance with Method/SOP requirements as appropriate. Qualify outliers.	Lab Manager / Analyst	Accuracy/Bias	Acceptance criteria are specified in Table 28-10 and Table 28-111

Table 28-10: Recovery & Precision Limits (Soil)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
Acenaphthene	20	43-113
Acenaphthylene	20	41-114
Anthracene	20	59-115
Benz[a]anthracene	20	62-122
Benzo[a]pyrene	20	56-113
Benzo[b]fluoranthene	20	43-138
Benzo[g,h,i]perylene	20	47-143
Benzo[k]fluoranthene	20	52-138
Chrysene	20	64-119
Dibenz[a,h]anthracene	20	59-133
Fluoranthene	20	64-122
Fluorene	20	46-114
Indeno[1,2,3-c,d]pyrene	20	59-132
2-Methylnaphthalene	20	44-120
Naphthalene	20	47-108
Phenanthrene	20	42-122
Pyrene	20	64-117
2-Fluorobiphenyl	NA	35-141
Terphenyl-d14	NA	64-141

Table 28-11: Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD and LCS)
Acenaphthene	20	48-104
Acenaphthylene	20	44-109
Anthracene	20	49-112
Benz[a]anthracene	20	63-109
Benzo[a]pyrene	20	51-98
Benzo[b]fluoranthene	20	41-139
Benzo[g,h,i]perylene	20	44-124
Benzo[k]fluoranthene	20	58-125
Chrysene	20	62-115
Dibenz[a,h]anthracene	20	55-124
Fluoranthene	20	65-112
Fluorene	20	49-108
Indeno[1,2,3-c,d]pyrene	20	54-125
2-Methylnaphthalene	20	47-103
Naphthalene	20	42-107
Phenanthrene	20	50-109
Pyrene	20	64-109
1,4-Dioxane	20	10-79
2-Fluorobiphenyl	NA	19-123
Terphenyl-d14	NA	58-130

Matrix: Soil/Aqueous
Analytical Group: GRO
Analytical Method/SOP: 8015B/ WI-PGH-O-003-0

TABLE 28-12: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per preparation batch (20 samples)	No target compounds >RL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
LCS	One LCS per preparation batch (20 samples)	Acceptance criteria are specified in Table 28-13 and Table 28-14	Reanalyze LCS once. If acceptable, report. Otherwise, evaluate and reprep and reanalyze the LCS and all samples in the associated prep batch for failed analytes, if sufficient sample material is available.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-13 and Table 28-14
MS/MSD for all analytes	One MS/MSD pair per preparation batch (20 samples)	Acceptance criteria are specified in Table 28-13 and Table 28-14	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze the native sample and MS/MSD pair as indicated.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-13 and Table 28-14
Surrogate standards	All field and QC samples.	Acceptance criteria are specified in Table 28-13 and Table 28-14	Determine if matrix effect or laboratory caused, then re-extract and reanalyze all affected samples in accordance with EPA Method requirements	Lab Manager / Analyst	Accuracy/Bias	Acceptance criteria are specified in Table 28-13 and Table 28-14

Table 28-13: Recovery & Precision Limits (Soil)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
C6-C10	30	65-135
C6-C12	30	65-135
4-Bromofluorobenzene	NA	60-125
1,1,1-Trifluorotoluene	NA	60-125

Table 28-14: Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (MS/MSD)
C6-C10	30	80-120
C6-C12	30	80-120
4-Bromofluorobenzene	NA	75-125
1,1,1-Trifluorotoluene	NA	75-125

Matrix: Soil/Aqueous
Analytical Group: DRO
Analytical Method/SOP: 8015B/ WI-PGH-O-002-0

TABLE 28-15: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per preparation batch (20 samples)	No target compounds >RL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
LCS	One LCS per preparation batch (20 samples)	Acceptance criteria are specified in Table 28-16 and Table 28-17	Reanalyze LCS once. If acceptable, report. Otherwise, evaluate and reprep and reanalyze the LCS and all samples in the associated prep batch for failed analytes, if sufficient sample material is available.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-16 and Table 28-17
MS/MSD for all analytes	One MS/MSD pair per preparation batch (20 samples)	Acceptance criteria are specified in Table 28-16 and Table 28-17	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze the native sample and MS/MSD pair as indicated.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-16 and Table 28-17
Surrogate standards	All field and QC samples.	Acceptance criteria are specified in Table 28-16 and Table 28-17	Determine if matrix effect or laboratory caused, then re-extract and reanalyze all affected samples in accordance with EPA Method requirements	Lab Manager / Analyst	Accuracy/Bias	Acceptance criteria are specified in Table 28-16 and Table 28-17

Table 28-16: Recovery & Precision Limits (Soil)

Analyte	Precision (RPD)		Recovery Limits
		Recovery Limits(LCS)	(LCS/MS/MSD)
Diesel Range Organics	25	80-120	65-135

Table 28-:17 Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)		Recovery Limits
		Recovery Limits(LCS)	(LCS/MS/MSD)
Diesel Range Organics	25	80-120	65-135

Matrix: Soil
Analytical Group: PCBs
Analytical Method/SOP: 8082A/ S-NY-O-314-rev.04

TABLE 28-18: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per preparation batch (20 samples)	No target compounds >RL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
LCS	One LCS per preparation batch (20 samples)	-Percent recovery must be within method limits of 70-130%.	Reanalyze LCS once. If acceptable, report. Otherwise, evaluate and reprep and reanalyze the LCS and all samples in the associated prep batch for failed analytes, if sufficient sample material is available.	Lab Manager / Analyst	Precision and Accuracy/Bias	-Percent recovery must be within method limits of 70-130%. - Must meet in house surrogate criteria*
MS/MSD for all analytes	One MS/MSD pair per preparation batch (20 samples)	70-130% recovery	Examine the project specific DQOs. Evaluate the data, note in report	Lab Manager / Analyst	Precision and Accuracy/Bias	70-130% recovery
Surrogate standards	All field and QC samples.	DCBP: 30-155% recovery TCMX: 38.9 – 143% recovery	Determine if matrix effect or laboratory caused, then re-extract and reanalyze all affected samples in accordance with EPA Method requirements	Lab Manager / Analyst	Accuracy/Bias	DCBP: 30-155% recovery TCMX: 38.9 – 143% recovery

Table 28-19: Recovery & Precision Limits (Soil)

Analyte	Precision (RPD)	Recovery Limits (LCS/MS/MSD)
Aroclor 1016	30	70-130
Aroclor 1221	30	70-130
Aroclor 1232	30	70-130
Aroclor 1242	30	70-130
Aroclor 1248	30	70-130
Aroclor 1254	30	70-130
Aroclor 1260	30	70-130
Aroclor 1262	30	70-130
Aroclor 1268	30	70-130
Decachlorobiphenyl (DCB)	NA	70-130
Tetrachlor-m-xylene (TCMX)	NA	70-130

Matrix: Aqueous
Analytical Group: PCBs
Analytical Method/SOP: 680/ SNYO040rev08 - PCBs by GCMS – FINAL

TABLE 28-20: Laboratory QC Samples Table

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per preparation batch (20 samples)	No target compounds >RL	Verify instrument clean (evaluate calibration blank & samples prior to method blank), then reanalyze. Evaluate to determine if systematic issue within laboratory, correct, then re-prepare and reanalyze the method blank and all samples processed with the contaminated blank in accordance with method/SOP requirements	Lab Manager / Analyst	Accuracy/Bias Contamination	No target compounds >RL

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Internal Standard	During acquisition of calibration standard, samples, and QC check samples	Areas within 30% to most recent calibration standard for each sample and QC sample	Identify problem. Reanalyze all affected samples	Lab Manager / Analyst	Precision and Accuracy/Bias	Areas within 30% to most recent calibration standard for each sample and QC sample
LCS	One LCS per preparation batch (20 samples)	Acceptance criteria are specified in Table 28-21	Reanalyze LCS once. If acceptable, report. Otherwise, evaluate and reprep and reanalyze the LCS and all samples in the associated prep batch for failed analytes, if sufficient sample material is available.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-21

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
MS/MSD for all analytes	One MS/MSD pair per preparation batch (20 samples)	Acceptance criteria are specified in Table 28-21	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze the native sample and MS/MSD pair as indicated.	Lab Manager / Analyst	Precision and Accuracy/Bias	Acceptance criteria are specified in Table 28-21
Surrogate standards	All field and QC samples.	Acceptance criteria are specified in Table 28-21	Determine if matrix effect or laboratory caused, then re-extract and reanalyze all affected samples in accordance with EPA Method requirements	Lab Manager / Analyst	Accuracy/Bias	Acceptance criteria are specified in Table 28-21

Table 28-21: Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	(LCS/MS/MSD)
Monochlorobiphenyl	40	60-140
Dichlorobiphenyl	40	60-140
Trichlorobiphenyl	40	60-140
Tetrachlorobiphenyl	40	60-140

Pentachlorobiphenyl	40	60-140
Hexachlorobiphenyl	40	60-140
Heptachlorobiphenyl	40	60-140
Octachlorobiphenyl	40	60-140
Nonachlorobiphenyl	40	60-140
Decachlorobiphenyl	40	60-140
Decachlorobiphenyl (C13 Labelled)	NA	60-140
Tetrachlor-m-xylene (TCMX)	NA	60-140

Matrix: Soil/Aqueous
Analytical Group: Metals
Analytical Method/SOP: 6010C/ PGH-M-008-16

TABLE 28-22: Laboratory QC Samples Table

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/Batch (20 samples)	No target analytes >RL	If sufficient sample is available, reanalyze samples. Qualify data as needed. Report results if sample results >10x blank result or sample results ND.	Analyst / Section Supervisor	Accuracy/Bias-Contamination	No target analytes >RL
Laboratory Control Sample	1/Batch (20 samples)	% Rec. ± 20 % of the true value	If sufficient sample is available, reanalyze samples. Qualify data as needed.		Accuracy/Bias	% Rec. ± 20 % of the true value
Matrix Spike/Matrix Spike Duplicate	1/Batch (20 samples)	%Rec. =75-125%; RPD < 20% .	Determine root cause; flag MS/MSD data; discuss in narrative.		Accuracy/Bias/ Precision	%Rec. =75-125%; RPD < 20% .
Post-Digestion Spikes	1/Batch (20 samples)	%Rec. =80-120%	Discuss in case narrative.	Analyst / Section Supervisor	Accuracy/Bias	%Rec. =80-120%
Dilution Test	1/Batch (20 samples)	%D ± 10%	Discuss in case narrative	Analyst / Section Supervisor		%D ± 10%

Table 28-23: Recovery & Precision Limits (Soil and Aqueous)

Analyte	Precision (RPD)	Recovery Limits Recovery Limits (LCS/LCSD)	Recovery Limits (MS/MSD)
Aluminum	20	80 - 120	75 - 125
Antimony	20	80 - 120	75 - 125
Arsenic	20	80 - 120	75 - 125
Barium	20	80 - 120	75 - 125
Beryllium	20	80 - 120	75 - 125
Cadmium	20	80 - 120	75 - 125
Chromium	20	80 - 120	75 - 125
Cobalt	20	80 - 120	75 - 125
Copper	20	80 - 120	75 - 125
Iron	20	80 - 120	75 - 125
Lead	20	80 - 120	75 - 125
Manganese	20	80 - 120	75 - 125
Nickel	20	80 - 120	75 - 125
Selenium	20	80 - 120	75 - 125

Analyte	Precision (RPD)	Recovery Limits Recovery Limits (LCS/LCSD)	Recovery Limits (MS/MSD)
Silver	20	80 - 120	75 - 125
Thallium	20	80 - 120	75 - 125
Vanadium	20	80 - 120	75 - 125
Zinc	20	80 - 120	75 - 125

Matrix: Soil/Aqueous
Analytical Group: Mercury
Analytical Method/SOP: 7470A/7471B NIOSH 6009/ PGH-M-017-5/ HGVAPOR

TABLE 28-24: Laboratory QC Samples Table (Soil and Aqueous)

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/Batch (20 samples)	No target analytes >RL	If sufficient sample is available, reanalyze samples. Qualify data as needed. Report results if sample results >10x blank result or sample results ND.	Analyst / Section Supervisor	Accuracy/Bias-Contamination	No target analytes >RL
Laboratory Control Sample	1/Batch (20 samples)	% Rec. ± 20 % of the true value	If sufficient sample is available, reanalyze samples. Qualify data as needed.		Accuracy/Bias	% Rec. ± 20 % of the true value
Matrix Spike/Matrix Spike Duplicate	1/Batch (20 samples)	%Rec. =75-125%; RPD < 20%	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze the native sample and MS/MSD pair as indicated.		Accuracy/Bias/ Precision	%Rec. =75-125%; RPD < 20%

Matrix: Soil/Aqueous
Analytical Group: Hexavalent Chromium
Analytical Method/SOP: 7196A/ PGH-I-012-10

TABLE 28-25: Laboratory QC Samples Table (Soil and Aqueous)

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/Batch (20 samples)	No target analytes >RL	If sufficient sample is available, reanalyze samples. Qualify data as needed. Report results if sample results >10x blank result or sample results ND.	Analyst / Section Supervisor	Accuracy/Bias-Contamination	No target analytes >RL
Laboratory Control Sample	1/Batch (20 samples)	% Rec. ± 20 % of the true value	If sufficient sample is available, reanalyze samples. Qualify data as needed.		Accuracy/Bias	% Rec. ± 20 % of the true value
Laboratory Duplicates	1/Batch (20 samples)	RPD <15% for aqueous samples; 20% for solid samples	Document in narrative		Accuracy/Bias/ Precision	RPD <15% for aqueous samples; 20% for solid samples
Matrix Spike (Soluble)	1/Batch (20 samples)	%Rec. =85-115%;	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze entire sample batch		Accuracy/Bias	%Rec. =85-115%;
Matrix Spike (Insoluble for solid matrix only)	1/Batch (20 samples)	%Rec. =75-125%	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze entire sample batch		Accuracy/Bias	%Rec. =75-125%
Post-Digestion Spike (solid matrix only)	1/Batch (20 samples)	%Rec. =85-115%	Document in narrative		Accuracy/Bias	%Rec. =85-115%

Matrix: Soil/Aqueous
Analytical Group: Cyanide
Analytical Method/SOP: 9012 PGH-I-053-12

TABLE 28-26: Laboratory QC Samples Table (Soil and Aqueous)

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/Batch (20 samples)	No target analytes >RL	If sufficient sample is available, reanalyze samples. Qualify data as needed. Report results if sample results >10x blank result or sample results ND.	Analyst / Section Supervisor	Accuracy/Bias-Contamination	No target analytes >RL
Laboratory Control Sample	1/Batch (20 samples)	% Rec. ± 10 % of the true value	Reanalyze samples. Footnote sample results as needed.		Accuracy/Bias	% Rec. ± 10 % of the true value
Laboratory Duplicates	1/Batch (20 samples)	RPD <20%	Reanalyze samples. Footnote sample results as needed.		Accuracy/Bias/ Precision	RPD <20%
Matrix Spike	1/Batch (20 samples)	%Rec. =90-110%	Review the spike results. Footnote sample results indicating matrix interferences		Accuracy/Bias	%Rec. =90-110%

Matrix: Soil/Aqueous
Analytical Group: Oil and Grease
Analytical Method/SOP: PGH-I-042-8 (1664A)/ PGH-I-052-7 (9071B)

TABLE 28-27: Laboratory QC Samples Table (Soil and Aqueous)

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/Batch (20 samples)	No Target Compounds>RL	If sufficient sample is available, reanalyze samples. Qualify data as needed. Report results if sample results >10x blank result or sample results ND.	Analyst / Section Supervisor	Accuracy/Bias-Contamination	No Target Compounds>RL
Laboratory Control Sample	1/Batch (20 samples)	Acceptance criteria are specified in Table 28-27 and Table 28-28	If sufficient sample is available, reanalyze samples. Qualify data as needed.		Accuracy/Bias	Acceptance criteria are specified in Table 28-27 and Table 28-28
Laboratory Duplicates	1/Batch (20 samples)	Acceptance criteria are specified in Table 28-27 and Table 28-28	Document in narrative		Accuracy/Bias/ Precision	Acceptance criteria are specified in Table 28-27 and Table 28-28
Matrix Spike	1/Batch (20 samples)	Acceptance criteria are specified in Table 28-27 and Table 28-28	Examine the project specific DQOs. Evaluate the data, and re-prepare/reanalyze the native sample MS/MSD as indicated.		Accuracy/Bias	Acceptance criteria are specified in Table 28-27 and Table 28-28

Table 28-28: Recovery & Precision Limits (Soil)

Analyte	Precision (RPD)	Recovery Limits (LCS)	Recovery Limits (MS)
Oil and Grease	20	85-115%	85-115%

Table 28-29: Recovery & Precision Limits (Aqueous)

Analyte	Precision (RPD)	Recovery Limits (LCS)	Recovery Limits (MS)
Oil and Grease	34	78-114% (HEM) 64-132% (SGT HEM)	78-114% (HEM) 64-132% (SGT HEM)

Matrix: Soil
Analytical Group: Dioxins and Furans
Analytical Method/SOP: S-MN-H-001-Rev.25

TABLE 28-27: Laboratory QC Samples Table (Soil)

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per analytical batch (20 samples) (8290)	No PCDDs/PCDFs >RL	If the contamination appears to be instrument related, correct the problem, analyze a solvent blank, and reanalyze the method blank before proceeding with samples. If the contamination appears to be from the extraction or enrichment steps, the analysis of samples may continue. If the sample shows similar contamination it must be re-extracted, if possible. All associated sample results must be qualified for method blank contamination when any analyte is detected in the method blank at 10% or more of the sample concentration. If the method blank shows no contamination above the reporting level calibration solution, analysis of samples may continue. However, all associated sample results must be qualified for method blank contamination when any analyte is detected in the method blank at 10% of more of the sample concentration	Lab Manager / Analyst	Accuracy/Bias Contamination	No PCDDs/PCDFs >RL

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
MS/MSD	One MS/MSD per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-28 and	Recoveries of selected analytes outside theacceptable range do not invalidate the databut provide information, which is used by thelaboratory to monitor recovery trends and toassure optimization of the method. This isparticularly true of MS/MSD recoverieswhere native PCDD/PCDF are subject to theeffects of the sample source. Data must bequalified accordingly on the final report.			

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD)	One LCS per analytical/preparation batch (20 samples)	Acceptance criteria are specified in Table 28-28.	If the recoveries are not within the control limits, data must be evaluated to determine the impact on the associated samples. If it is determined that the instrument may be the cause of the outlier, the QC must be reanalyzed to confirm results as well as any associated samples that may have been impacted by the instrumentation failure. If it is determined that the cause is due to poor extraction, all associated samples must be re-extracted and reanalyzed or qualified accordingly		Accuracy/Bias	Acceptance criteria are specified in Table 28-28.

Table 28-28: Recovery & Precision Limits (Soil)

Analyte	Recovery Limits (LCS)	Recovery Limits (MS)	Precision (RPD)
2,3,7,8-TCDF	70-130	70-130	20
2,3,7,8-TCDD	70-130	70-130	20
1,2,3,7,8-PeCDF	70-130	70-130	20
2,3,4,7,8-PeCDF	70-130	70-130	20
1,2,3,7,8-PeCDD	70-130	70-130	20
1,2,3,4,7,8-HxCDF	70-130	70-130	20
1,2,3,6,7,8-HxCDF	70-130	70-130	20
2,3,4,6,7,8-HxCDF	70-130	70-130	20
1,2,3,7,8,9-HxCDF	70-130	70-130	20
1,2,3,4,7,8-HxCDD	70-130	70-130	20
1,2,3,6,7,8-HxCDD	70-130	70-130	20
1,2,3,7,8,9-HxCDD	70-130	70-130	20
1,2,3,4,6,7,8-HpCDF	70-130	70-130	20
1,2,3,4,7,8,9-HpCDF	70-130	70-130	20
1,2,3,4,6,7,8-HpCDD	70-130	70-130	20
OCDF	70-130	70-130	20
OCDD	70-130	70-130	20
Total TCDF	70-130	70-130	20
Total TCDD	70-130	70-130	20
Total PeCDF	70-130	70-130	20
Total PeCDD	70-130	70-130	20
Total HxCDF	70-130	70-130	20

Total HxCDD	70-130	70-130	20
Total HpCDF	70-130	70-130	20
Total HpCDD	70-130	70-130	20

QAPP Worksheet #29: Project Documents and Records
(UFP-QAPP Manual Section 3.5.1)
(EPA 2106-G-05 Section 2.2.8)

Sample Collection and Field Records			
Record	Generation	Verification	Storage location/archival
Field logs or data collection sheets including well sampling forms, hydraulic test records, XRF data collection form, test pit log, etc.	Field Personnel	Task Managers	Project File
Chain-of-Custody Forms	Field Personnel	Task Managers	Project File
Boring Logs and Well Construction Logs	Field Personnel	Task Managers	
Air Bills	Field Personnel	Project Manager	Project File
Contractor Daily QC Reports	Task Manager	Project Manager	Project File
Deviations	Task Manager	Quality Manager	Project File
Corrective Action Reports	Task Manager/Project Manager	Quality Manager	Project File

*Task Manager refers to EAG, ARM, Key, ARC, and/or any other contract personnel managing specific investigations. The responsible Task Manager will be identified in each task Work Plan.

Project Assessments			
Record	Generation	Verification	Storage location/archival
Field audit checklists	Task Manager	Project Manager	Project File
Data verification checklists	Task Manager	Project Manager	Project File

Project Assessments			
Record	Generation	Verification	Storage location/archival
Data validation report	Project Chemist	Project Manager	Project File
Data usability assessment report	Project Chemist	Project Manager	Project File

Laboratory Records			
Record	Generation	Verification	Storage location/archival
Sample Receipt & COC Records	Contract Laboratory Personnel	Project Chemist	Project File
Instrument Calibration Logs	Contract Laboratory Personnel	Project Chemist	Project File
Sample Prep Logs	Contract Laboratory Personnel	Project Chemist	Project File
Equipment Maintenance Logs	Contract Laboratory Personnel	Project Chemist	Project File
Corrective Action Forms	Contract Laboratory Personnel	Project Chemist	Project File
QC Results	Contract Laboratory Personnel	Project Chemist	Project File
Data Reports	Contract Laboratory Personnel	Project Chemist	Project File
EDDs	Contract Laboratory Personnel	Project Chemist	Project File

Laboratory Data Deliverables—Level 2 Data Package
Cover Letter
Certifications Page
Sample Summary Page (optional)
Sample Analyte Count Page (optional)
Project Narrative Pages (standard or custom)
Analytical Results (surrogate recoveries where applicable)

Laboratory Data Deliverables—Level 2 Data Package
Quality Control Data tables (method blank, LCS/LCSD, DUP, MS/MSD where applicable)
Qualifiers Page
Quality Control Data Cross Reference Table (optional)
COC and SCUR

Laboratory Data Deliverables—Level 4 Data Package (includes all Level 2 items)				
Item	GC/MS Reportable Data	GC Reportable Data	Wet Chemistry Reportable Data	Metals (ICP/Hg) Reportable Data
Surrogate Summary	X	X		
Method Blank Summary	X	X	X	X
Tune report (Target Summary)	X			
Analytical Sequence (Run Log)	X	X	X	X
Internal Standard Summary	X			
Initial Calibration				
Initial Calibration Summary plus all levels	X	X	X	
ICV—Second Source verification of ICAL	X	X	X	X
Continuing Calibration Summary (Target forms)	X	X	X	X
Sample Chromatograms and quantitation reports	X	X		
Mass Spectra, including reference spectra	X			
Sample preparation/extraction forms where applicable	X	X	X	X
Instrument raw data printouts for all samples, standards and QC samples			X	X
QL Check Standard Summary			X	X
Initial Calibration Verification and Continuing Calibration Verification			X	X

Initial Calibration Blank and Continuing Calibration Blank			X	X
Interference Check Sample				X
Serial Dilution				X
Method Detection Limit	X	X	X	X
Preparation Log				X
Analysis Run Log				X
Tunes (Form 14)				

See Appendix C For Complete Data Management Plan

QAPP Worksheet #31, 32 & 33: Assessments and Corrective Action
(UFP-QAPP Manual Sections 4.1.1 and 4.1.2)
(EPA 2106-G-05 Section 2.4 and 2.5.5)

Assessments:

Assessment Type	Responsible Party & Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable due date
Readiness Review	Task Managers – ARM/EAG/KEY/ARC	One Assessment prior to the commencing field work for a given investigation or phase of investigation		Readiness Review Sign-in sheet	24 hours following assessment
Field Sampling TSA	Task Managers – ARM/EAG/KEY/ARC	One each on first day of soil, soil-gas, sediment and groundwater sampling episodes		TSA Memorandum and Audit Checklist	24 hours following assessment
Field Progress Reports	Task Managers - ARM/EAG/KEY/ARC	Daily Field Reports shall be compiled and reviewed during field activities.		Task Managers shall report to EAG Project Manager, at a minimum, on a weekly basis.	Weekly

QAPP Worksheet #34: Data Verification and Validation Inputs
(UFP-QAPP Manual Section 5.2.1 and Table 9)
(EPA 2106-G-05 Section 2.5.1)

Item	Description	Verification (completeness)	Validation (conformance to specifications)
Planning Documents/Records			
1	Approved QAPP	**X**	
2	Contract	**X**	
4	Field SOPs	**X**	
5	Laboratory SOPs	**X**	
Field Records			
6	Field logbooks	**X**	**X**
7	Equipment calibration records	**X**	**X**
8	Chain-of-Custody Forms	**X**	**X**
9	Sampling diagrams/surveys	**X**	**X**
10	Drilling logs	**X**	**X**
11	Geophysics reports	**X**	**X**
12	Relevant Correspondence	**X**	**X**
13	Change orders/deviations	**X**	**X**
14	Field audit reports	**X**	**X**
15	Field corrective action reports	**X**	**X**
Analytical Data Package			
16	Cover sheet (laboratory identifying information)	**X**	**X**
17	Case narrative	**X**	**X**
18	Internal laboratory chain-of-custody	**X**	
19	Sample receipt records	**X**	**X**
20	Sample chronology (i.e. dates and times of receipt, preparation, & analysis)	**X**	
21	Communication records	**X**	
22	Project-specific PT sample results	**X**	
23	LOD/LOQ establishment and verification	**X**	**X**
24	Standards Traceability	**X**	
25	Instrument calibration records	**X**	**X**
26	Definition of laboratory qualifiers	**X**	**X**
27	Results reporting forms	**X**	**X**
28	QC sample results	**X**	**X**
29	Corrective action reports	**X**	
30	Raw data	**X**	
31	Electronic data deliverable	**X**	

QAPP Worksheet #35: Data Verification Procedures
(UFP-QAPP Manual Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

Records Reviewed	Requirement Documents	Process Description	Responsible Person, Organization
Field Logbook	QAPP, SOPs	Field notes will be prepared daily by the field operations leader. Verify that all planned samples were collected and that sample collection locations are documented. Record date and time of arrival at the sampling location and identify the individual collecting the sample. Any use of field equipment should be listed, as well as associated maintenance and operation procedures. This record should identify any calibration times and the person preparing the sample blank, as well as any other pertinent observations. Any deviation from the plan, and reasons for the deviation, will be noted. Logbooks will be placed in the project file upon completion of field work.	Daily - Project Manager At conclusion of field activities - Project QA Manager
Field Data Sheets	QAAP, SOPs	All sample collection will be documented on the appropriate field data sheets. Once in sample containers, the sample ID, location, date, and time of collection will be recorded on the label. The field data sheets should be completed and verified for all field samples, including indoor air, sub-slab soil gas, sediment, surface water, groundwater, low flow groundwater, surface soil, and sub-surface soil.	Daily - Project Manager At conclusion of field activities - Project QA Manager
Chain-of-custody Forms	QAPP, SOPs	COC forms will be reviewed for completeness and accuracy. COC records will be verified against the logbook and samples stored in the cooler. COCs will be signed and copies of the forms will be retained within the project file.	Daily - Field Crew Chief At conclusion of field activities - Project Chemist

Laboratory Deliverable	QAPP	The laboratory deliverables will be verified to ensure that all records specified in the QAPP and that necessary signatures and dates are present. Sample receipt records will be reviewed to ensure sample condition upon receipt was noted, and any missing/broken sample containers were noted and reported according to plan. The data package will be compared to the COCs to verify that results were provided for all collected samples. The data package case narrative will be reviewed to ensure all QC exceptions are described.	Before release – Laboratory QAM Upon receipt - Project Chemist
Audit Reports, Corrective Action Reports	QAPP	All planned audits will be conducted. Audits of field collection procedures are conducted at the start of each type of sample collection of each investigation. The reports are reviewed, and corrective action should be implemented and verified for any deficiencies noted. Audits of analytical data will be completed during the data usability assessment (Worksheet #37) and any necessary corrective action will be implemented.	Project QAM

QAPP Worksheet #36
Data Validation Procedures
(UFP-QAPP Manual Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

Data Validator: Environmental Data Quality, Inc.

Analytical Group/Method:	Volatile Organic Compounds – TO-15	Volatile Organic Compounds - SW-846 8260B
Data deliverable requirements:	Level IV (pdf); EDD	Level IV (pdf); EDD
Analytical specifications:	SOP S-LI-O-022-rev.01	SOP PGH-O-015-9
Measurement performance criteria:	WS 12	WS 12
Percent of data packages to be validated:	100%	100%
Percent of raw data reviewed:	0%	0%
Percent of results to be recalculated:	0%	0%
Validation procedure:	USEPA-540-R-08-01	USEPA-540-R-08-01
Validation code (*see attached table):	S2bVM	S2bVM
Electronic validation program/version:	NA	NA

Data Validator: Environmental Data Quality, Inc.

Analytical Group/Method:	Semivolatile Organic Compounds - SW-846 8270D	Polyaromatic Hydrocarbons by Selective Ion Monitoring (PAHS by SIM), 8270D SIM
Data deliverable requirements:	Level IV (pdf); EDD	Level IV (pdf); EDD
Analytical specifications:	SOP PGH-O-001-8	SOP PGH-O-023-5
Measurement performance criteria:	WS 12	WS 12
Percent of data packages to be validated:	100%	100%
Percent of raw data reviewed:	0%	0%
Percent of results to be recalculated:	0%	0%
Validation procedure:	USEPA-540-R-08-01	USEPA-540-R-08-01
Validation code (*see attached table):	S2bVM	S2bVM
Electronic validation program/version:	NA	NA

Data Validator: Environmental Data Quality, Inc.

Analytical Group/Method:	Polychlorinated Biphenyls - SW-846 8082, 680	GRO/DRO – SW-846 8015B
Data deliverable requirements:	Level IV (pdf); EDD	Level IV (pdf); EDD
Analytical specifications:	SOPs WI-PGH-O-038-0 (8082); S-NY-O-040-rev.08 - PCBs by GCMS - FINAL (680)	SOPs WI-PGH-O-003-0 (GRO); WI-PGH-O-002-0 (DRO)
Measurement performance criteria:	WS 12	WS 12
Percent of data packages to be validated:	100%	100%
Percent of raw data reviewed:	0%	0%
Percent of results to be recalculated:	0%	0%
Validation procedure:	USEPA-540-R-08-01	USEPA-540-R-08-01
Validation code (*see attached table):	S2bVM	S2bVM
Electronic validation program/version:	NA	NA

Data Validator: Environmental Data Quality, Inc.

Analytical Group/Method:	Metals – SW-846 6010C/7470A/7471A/6009	Cyanide - SW-846 9012
Data deliverable requirements:	Level IV (pdf); EDD	Level IV (pdf); EDD
Analytical specifications:	SOPs PGH-M-008-16 (ICP); PGH-M-017-5 (Hg); HGAVAPOR	SOP PGH-I-053-12
Measurement performance criteria:	WS 12	WS 12
Percent of data packages to be validated:	100%	100%
Percent of raw data reviewed:	0%	0%
Percent of results to be recalculated:	0%	0%
Validation procedure:	USEPA-540-R-10-011	USEPA-540-R-10-011
Validation code (*see attached table):	S2bVM	S2bVM
Electronic validation program/version:	NA	NA

Data Validator: Environmental Data Quality, Inc.

Analytical Group/Method:	Hexavalent Chromium – SW-846 7196A/218.6	Oil and Grease – SW-846 9071B/*1664A*
Data deliverable requirements:	Level IV (pdf); EDD	Level IV (pdf); EDD
Analytical specifications:	SOP PGH-I-012-10	SOPs PGH-I-052-7 (Solid); PGH-I-042-8 (Aqueous)
Measurement performance criteria:	WS 12	WS 12
Percent of data packages to be validated:	100%	100%
Percent of raw data reviewed:	0%	0%
Percent of results to be recalculated:	0%	0%
Validation procedure:	USEPA-540-R-10-011	USEPA-540-R-10-011
Validation code (*see attached table):	S2bVM	S2bVM
Electronic validation program/version:	NA	NA

Validation Code and Label Identifier Table (To be attached to the QAPP)

Validation Code*	Validation Label	Description/Reference
S1VE	Stage 1 Validation Electronic	EPA 540-R-08-005
S1VM	Stage 1 Validation Manual	
S1VEM	Stage 1 Validation Electronic and Manual	
S2aVE	Stage 2a Validation Electronic	
S2aVM	Stage 2a Validation Manual	
S2aVEM	Stage 2a Validation Electronic and Manual	
S2bVE	Stage 2b Validation Electronic	
S2bVM	Stage 2b Validation Manual	
S2bVEM	Stage 2b Validation Electronic and Manual	
S3VE	Stage 3 Validation Electronic	
S3VM	Stage 3 Validation Manual	
S3VEM	Stage 3 Validation Electronic and Manual	
S4VE	Stage 4 Validation Electronic	
S4VM	Stage 4 Validation Manual	
S4VEM	Stage 4 Validation Electronic and Manual	
NV	Not Validated	

The following data qualifiers will be applied during data validation by a third party. Potential impacts on project-specific data quality objectives will be discussed in the data validation report.

NM – Measurement Performance Criteria contained in WS 12 were not met.
J – The result is an estimated value. The nature of the bias will be discussed in the data validation report.
E – Erroneous result (e.g., improper calculation, peak integration, etc.)

QAPP Worksheet #37: Data Usability Assessment
(UFP-QAPP Manual Section 5.2.3 including Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

Project Manager: James Calenda
Risk Assessor: Varies
Statistician: Sean McCarthy
Project QAM: Russell Becker
Project Chemist: Shawne Rodgers

Objective of the data usability assessment:

The assessment will evaluate the usability of data gathered during the project, including data collected on small and large scales. This includes data that may be specific to individual samples or analytes, as well as overall environmental datasets from large sampling events.

Summary of the usability assessment process:

The personnel listed above will be primarily responsible for completion of the data usability assessment. These individuals will perform the verification procedures listed in Worksheet #35 and the validation procedures included in Worksheet #36. The practices will confirm the reliability of fieldwork exercises and analytical methods, evaluating the compliance with the QAPP and other supporting documents. The evaluation reports will be recorded in the QA project documents listed in Worksheet #29. The DQIs used to evaluate data quality (accuracy/bias, precision, representativeness, completeness, comparability, and sensitivity) are described in Worksheet #12, including the formulas used for quantitative metrics and the data quality requirements for each indicator. Laboratory-specific quantitation limits are presented in Worksheet #15.

Description of the evaluative procedure:

The usability assessment can only be performed on data of known quantity, and thus is considered the final step in data evaluation. The data usability assessment proceeds following the verification and validation procedures mentioned above. The process will examine the quality control elements of accuracy/bias, precision, representativeness, completeness, comparability, and sensitivity, and address any data gaps resulting from incomplete or unreliable sampling.

First, sampling and analytical activities will be reviewed and compared to the appropriate project documents. Any estimated or rejected datum shall be documented.

Second, the DQIs for the dataset will be determined for comparison to the planned or expected performance. This critical step will determine whether any corrective action may be necessary, including resampling of sites or reanalysis of samples. If correction is not possible, the data evaluation personnel will make final determinations concerning whether data is usable with respect to the DQOs.

Third, achievement of the DQOs is evaluated with respect to the data of interest. Following the documentation of any data limitations, the applicability of the data to achieve the DQOs can be determined based on several considerations:

- Do the data describe the extent of potential source areas of hazardous substances?
- Do the data describe the extent to which hazardous substances have migrated or may migrate?
- Do the data allow for the characterization of factors that affect migration or distribution of hazardous substances, such as physical barriers or water table changes?
- Do the data convey valuable information for designing removal or disposal systems?
- Do the data describe any key characteristic of the hazardous substance, such as environmental availability or toxicity, not previously known?
- Do the data describe any other factors relating to hazardous substances or environmental setting which may become pertinent during the project lifetime?

The following table contains additional information and description of the planned processing of environmental datasets using statistical methods.

Step 1	**Review the project's objectives and sampling design.** Based on the data received, the DQOs for each investigation area, as well as any site-wide DQOs will be revisited, to evaluate if the collected verified data can be used to achieve or approach study objects.
Step 2	**Review the data verification and data validation outputs.** Verified data will be tabulated, evaluated and modelled spatially/temporally to identify any preliminary conclusions that can be drawn from the data. Particular attention will be given towards identifying any potential data gaps that may exist due to either deviations from the project planning or simply unforeseen conditions. If a significant number of data are found to be unacceptable, QA/QC measures will be thoroughly evaluated and determinations will be made with regards to recollection or supplementing completed investigations.
Step 3	**Verify the assumptions of the selected statistical method. It may not be necessary to conduct statistical analysis of the data. For example, the maximum concentrations from a given data set are initially compared to PALs to determine which chemicals are constituents of Concern (COCs) for that particular data set/parcel.** However, statistical Analysis may be used to evaluate various hypotheses regarding the data. A number of statistical methods can be used to test these hypotheses; however, method selection will depend upon characteristics of the sample population (sample size, sample distribution, variations from background conditions, et cetera). In general, a major portion of the collected data will be constituent concentrations and subsequently be compared to action levels. The statistical approach will be designed to test the general hypothesis "Parameter X is below the corresponding Action Level". This hypothesis can also apply to data being collected for the purpose of remedial alternative evaluation, where performance criteria, et cetera is used in lieu of action level. If needed, the statistical methods will be selected following the receipt of the validated data.

Step 4	**Implement the statistical method.** If a statistical analysis is to be employed, the underlying assumptions for the statistical methods will be evaluated. Hypotheses will be reevaluated after statistical analysis to assess their strength. Uncertainty tolerances will be considered.
Step 5	**Document data usability and draw conclusions.** A determination will be made on whether the data can be used as intended, considering implications of deviations and corrective actions. Any data limitations will be identified. The performance of the sampling design will be assessed via data quality indicators. The CSM will be updated and conclusions will be recorded in a data usability summary report table.

FIGURES

N

ARM Group Inc.
Earth Resource Engineers and Consultants

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Feet

Carve-out Area
Northern Corrective Action Area
Southern Corrective Action Area
Private Property

Sparrows Point Carve-out and Corrective Action Areas

August 18, 2015

EnviroAnalytics Group	Sparrows Point Terminal
ARM Project 150241M	Baltimore County, MD

Figure
1

TABLES

Table 1
Crosswalk: UFP-QAPP Workbook to 2106-g-05 QAPP

Optimized UFP-QAPP Worksheets		**2106-G-05 QAPP Guidance Section**	
1 & 2	Title and Approval Page	2.2.1	Title, Version, and Approval/Sign-Off
3 & 5	Project Organization and QAPP Distribution	2.2.3	Distribution List
		2.2.4	Project Organization and Schedule
4 , 7 & 8	Personnel Qualifications and Sign-off Sheet	2.2.1	Title, Version, and Approval/Sign-Off
		2.2.7	Special Training Requirements and Certification
6	Communication Pathways	2.2.4	Project Organization and Schedule
9	Project Planning Session Summary	2.2.5	Project Background, Overview, and Intended Use of Data
10	Conceptual Site Model	2.2.5	Project Background, Overview, and Intended Use of Data
11	Project/Data Quality Objectives	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
12	Measurement Performance Criteria	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
13	Secondary Data Uses and Limitations	Chapter 3	QAPP ELEMENTS FOR EVALUATING EXISTING DATA
14 & 16	Project Tasks & Schedule	2.2.4	Project Organization and Schedule
15	Project Action Limits and Laboratory-Specific Detection / Quantitation Limits	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
17	Sampling Design and Rationale	2.3.1	Sample Collection Procedure, Experimental Design, and Sampling Tasks
18	Sampling Locations and Methods	2.3.1	Sample Collection Procedure , Experimental Design, and Sampling Tasks
		2.3.2	Sampling Procedures and Requirements
19 & 30	Sample Containers, Preservation, and Hold Times	2.3.2	Sampling Procedures and Requirements
20	Field QC	2.3.5	Quality Control Requirements
21	Field SOPs	2.3.2	Sampling Procedures and Requirements
22	Field Equipment Calibration, Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
23	Analytical SOPs	2.3.4	Analytical Methods Requirements and Task Description

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
24	Analytical Instrument Calibration	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
26 & 27	Sample Handling, Custody, and Disposal	2.3.3	Sample Handling, Custody Procedures, and Documentation
28	Analytical Quality Control and Corrective Action	2.3.5	Quality Control Requirements
29	Project Documents and Records	2.2.8	Documentation and Records Requirements
31, 32 & 33	Assessments and Corrective Action	2.4	ASSESSMENTS AND DATA REVIEW (CHECK)
		2.5.5	Reports to Management
34	Data Verification and Validation Inputs	2.5.1	Data Verification and Validation Targets and Methods
35	Data Verification Procedures	2.5.1	Data Verification and Validation Targets and Methods
36	Data Validation Procedures	2.5.1	Data Verification and Validation Targets and Methods
37	Data Usability Assessment	2.5.2	Quantitative and Qualitative Evaluations of Usability
		2.5.3	Potential Limitations on Data Interpretation
		2.5.4	Reconciliation with Project Requirements

APPENDIX A

Field Standard Operating Procedures

Appendix A Table of Contents

SOP No. 001
INDOOR AIR SAMPLING
STANDARD OPERATING PROCEDURE
Rev. 03

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1 SCOPE

This Standard Operating Procedure (SOP) identifies the equipment and techniques used in the collection of time-integrated air samples in Summa canisters for the analysis of volatile organic compounds (VOCs).

2 EQUIPMENT

Equipment and materials necessary for the collection of indoor air samples include, at a minimum, the following:

- Laboratory supplied Summa canister(s)
  - Stainless Steel 6 L Summa canister(s), cleaned and certified (or batch certified), per EPA Method TO-15 guidelines.
- Laboratory supplied flow controller
  - Pre-set flow controller that maintains a constant mass flow rate over a specified period of time (8 hours).
- In-line particulate filter
  - A 2-µm sintered stainless steel shall be provided by the laboratory and present on the Summa canister or flow-controller.
- Vacuum gauge
  - Shall be provided by the laboratory.
  - Used to measure and record both the initial and final canister vacuum.
- Tubing.
  - To attach to the inlet of the flow controller in order to obtain samples from the breathing zone or a remote location.
  - Inert materials (e.g., stainless steel, copper, brass, polyvinyl chloride, high-density polyethylene) are recommended (OSWER 2015).
  - Can be a combination of the listed tubing types.
- Field Logbook
  - To record initial and final canister vacuums; collection start time and end time; sample identification; sample location; and any pertinent observations made by or reported to the sampler.

- Brass Cap and Plugs
  - Provided by the laboratory with the summa canister.
  - ¼" Swagelok.
  - Ensures no loss of vacuum due to a leaky valve or valve that is accidentally opened during handling.
  - Prevents dust and other particulate material from damaging the valve.
- Wrench(es)
  - 9/16" or adjustable wrench to assemble hardware.
  - 1/2" wrench may be needed if union connectors are employed.

3 PRELIMINARY SCREENING

An adequate background review should be conducted before sampling to obtain information on each structure from which a sample is to be collected. This review may be included in the project planning documentation. The background review should:

- Identify potential safety hazards;
- Identify conditions that may affect or interfere with the proposed testing;

Potential interference that is not considered representative of the ambient air conditions within the structure should be eliminated to the extent possible. These interferences may include:

- Ventilation not representative of typical ambient conditions;
- Exhaust from vehicles or mechanical equipment;
- Smoking in the interior space;
- The use of products or chemicals that may release VOCs to the ambient air.

Upon mobilization, the sampler should assess any potential conditions that may affect sampling results, record these conditions in the field logbook, and report said conditions to the Project Manager prior to sampling.

4 SAMPLING LOCATIONS

Indoor air samples should be collected in the breathing zone (approximately three (3) to six (6) feet above grade) to simulate seated or standing conditions. Sample locations shall be located as close as possible to the center of the interior space or in accordance with the locations provided in the approved work plan. To the extent possible, canisters should not be placed in areas of high humidity, near windows or heat registers. For every building where indoor air samples will be collected, there should be a least one outdoor air sample collected to provide background concentrations comparison. Ideally the outdoor sample should be collected upwind of the building(s) and away from obvious VOC sources (e.g., parked cars, vehicular traffic, mechanical

equipment, garages, et cetera) to account for potential background influences. This will provide assessment of ambient air impact on indoor air concentrations. The sample locations should be confirmed with the work plan, noted on an adequately detailed site map, and/or depicted in the field logbook. The frequency or necessity of duplicate sample location(s) should be specified in project planning documentation.

5 SAMPLING PROCEDURES

Pace Analytical Laboratories will supply all Summa Canisters, flow controllers, in-line particulate filters, and vacuum gauges. The sampler should inspect the equipment prior to mobilization, to ensure knowledge of assembly. If needed, specific instructions and/or diagrams for system assembly, if any, should be obtained from the laboratory supplying the canister(s). The initial canister vacuum should be verified by the laboratory, prior to shipment, to be 0.05 mm Hg (absolute pressure), or-30 inches of mercury (inHg or ”Hg) on the gauge. The sampler shall also inspect the canister prior to mobilization to identify any defects and/or loose fittings. The sampler will check the flow rate on the regulator and confirm the appropriate sampling time. Samples will be collected over an 8-hour period.

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sampler, shall be reported to the Project Manager prior to proceeding with field activities.

Sampler shall record the ambient temperature in the field logbook, immediately prior to sample collection.

In general, assembly of the sampling apparatus, sample collection, and documentation shall be performed as follows:

- Confirm that the valve is closed;
- Remove brass cap from the canister;
- Connect the flow controller (if provided separate from the Summa canister assembly), with attached vacuum gauge, to the canister utilizing a compression fitting;
- Using a wrench, ensure brass plug or cap on the intake end of the flow controller is attached and tightened, creating an airtight train, and quickly open and close the canister valve to check for leaks,
    - if the needle on the gauge drops, the train is not airtight – try refitting and/or tightening connections until the needle holds steady,
    - if gauge continues to drop, contact Project Manager for instructions on proceeding,
    - do not over tighten brass caps/plugs;
- Connect a sampling tube (if used) to the sample inlet on the filter/flow controller;

- Place the canister in the predetermined location and begin sampling by opening the canister valve as specified by the manufacturer and/or laboratory;
- Record the sample number, location, date, flow controller and canister serial numbers, initial vacuum reading, and start time in the field logbook,
    - the initial canister vacuum should be at least -25 inches of mercury (inHg or "Hg). If the initial canister vacuum is less than -25 inHg, (i.e., between 0 inHg and -24 inHg), report condition to the Project Manager.
- After sampling is complete, close the canister valve and record the end time and final canister vacuum in the field logbook and disassemble the flow controller/gauge,
    - do not over-tighten the valves or brass caps/plugs (i.e., hand-tighten and ¼ turn with a wrench for caps/plugs),
    - the final canister vacuum should generally be between -3 inHg and -10 inHg, and at a minimum be sub-atmospheric;
- Fill out canister sample tag only with indelible ink, making sure the sample ID and date of collection recorded on the sample tag matches what is recorded on the chain-of-custody (COC), and affix tag to canister; and
- Package the canisters and flow controllers in the laboratory-provided shipping container or box and transport to the laboratory, from which the canisters were rented, under COC protocol.

Sample management; including COC, handling, packing, and shipping procedures shall be in accordance with the procedures and requirements of *SOP No. 011 "Sample Handling, Packing, Shipping and Chain of Custody"*.

6 SAMPLE ANALYSIS

All air samples will be analyzed for VOCs by EPA Method TO-15. This method uses gas chromatography/mass spectrometry (GC/MS) to identify and quantify target VOCs. The technical holding time for method TO-15 is 14 days from collection.

7 REFERENCES

EPA (1999). *Compendium Method TO-15 – Determination of Volatile Organic Compounds (VOCs) in Ambient Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry.* Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air – 2nd Edition. EPA/625/R-96/010b. Center for Environmental Research Information, Office of Research and Development, United States Environmental Protection Agency. Cincinnati, OH. January, 1999.

ITRC (2007). *Vapor Intrusion Pathway: A Practical Guide.* Interstate Technology and Regulatory Council. Washington D.C.. January, 2007.

KDHE (2007). *Kansas Vapor Intrusion Guidance.* Bureau of Environmental Remediation, Division of Environment, Kansas Department of Health and Environment. Topeka, KS. June, 2007.

OSWER (2015). Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air.

SOP No. 002
SUB-SLAB SOIL GAS SAMPLING
STANDARD OPERATING PROCEDURE
Rev. 04

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1 SCOPE

This Standard Operating Procedure (SOP) identifies the equipment and techniques used in the collection of grab or time-integrated soil gas samples in Summa canisters for the analysis of volatile organic compounds (VOCs).

2 EQUIPMENT

The equipment for the collection of sub-slab soil gas samples may include the following:

2.1 Monitoring Point Installation

2.1.1 Temporary or Permanent Monitoring Point

- Core drill or hammer rotary drill with masonry bit
  - Core and/or bit diameter will be dependent upon project-specific requirements.
    - At a minimum, masonry bit should be 3/8" ø by 10" long.
- Extension cord(s)
- Field Logbook
- Hand-auger or single-piston slam bar (if required)
  - Used to extend borehole past bottom of concrete slab.
- Soil Gas Implant
  - 6" long, constructed of double woven stainless steel wire screen, or similar.
- Filter Sand
  - For backfill of annular space around soil gas implant.
- Bentonite clay
  - To create hydrated seal above the sand pack.
- Quick mix concrete (optional, for permanent monitoring point)
- Water
  - For hydration of the bentonite seal and concrete.
- Tubing
  - Flexible LDPE, Silicon, or PVC.

- Swagelok Fittings
  - Nut, Ferrule, and Plug.
  - To create a sealable fitting at sampling point inlet.
- PVC cleanout and plug
  - For permanent monitoring points.

2.1.2 Direct Push Installation

- Permanent or temporary monitoring points installed via direct push methods will utilize much of the same equipment presented in **Section 2.1.1.** These points should be installed in accordance with the recommendations presented in Technical Bulletin No. MK3098 9 (GPS, 2006) or most recent revision.

2.2 Sample Collection

Equipment and materials necessary for the collection of indoor air samples include, at a minimum, the following:

Summa canister sample collection

- Laboratory supplied Summa canister(s)
  - For time-integrated soil gas sampling.
  - Stainless Steel 6 L Summa canister(s), cleaned and certified (or batch certified), as per EPA Method TO-15 guidelines.
- Laboratory supplied flow controller
  - Pre-set flow controller that maintains a constant mass flow rate over a specified period of time (8 hours).
- In-line particulate filter
  - Shall be provided by the laboratory and present on the Summa canister or flow-controller.
- Vacuum gauge
  - Shall be provided by the laboratory.
  - Used to measure and record both the initial and final canister vacuum.
- Tubing
  - To attach to the inlet of the flow controller in order to obtain samples.
  - Inert materials (e.g., stainless steel, copper, brass, polyvinyl chloride, high-density polyethylene) are recommended (OSWER 2015).
  - Can be a combination of the listed tubing types.
- Field Logbook
  - To record initial and final canister vacuums; collection start time and end time; sample identification; sample location; and any pertinent observations made by or reported to the sampler.

- Brass Cap and Plugs
    - Provided by the laboratory with the summa canister.
    - ¼" Swagelok.
    - Ensures no loss of vacuum due to a leaky valve or valve that is accidentally opened during handling.
    - Prevents dust and other particulate material from damaging the valve.
- Wrench(es)
    - 9/16" or adjustable wrench to assemble hardware.
    - 1/2" wrench may be needed if union connectors are employed.
- Tedlar Bag
    - For leak testing.
    - 1-L
- 60 cc gas-tight syringe(s)
    - For purging of sampling point.
- Three way valve.
    - For purging of sampling point.
- Small garbage bag
- PID meter
- Sand filled hose
- Utility Knife
- Polyethylene Tubing
    - For leak testing.
- Silicon Tubing
    - For leak testing.
    - Hand-held helium detector (IonScience GasCheck 3000IS Gas Leak Detector).
- Helium Cylinder with regulator

3 SOIL GAS MONITORING POINT INSTALLATION

Soil gas monitoring point installation will vary, depending on project specific objectives. Sample locations shall be located in accordance with the locations provided in the approved work plan, or as close as possible to those locations. The following details procedures for the installation of temporary or permanent soil gas monitoring points.

- Where installing sampling points through a concrete slab or asphalt slab, a core drill or hammer rotary drill shall be utilized to drill a pilot hole through the concrete/asphalt;
- Once the pilot hole is installed, a hand auger or single piston slam bar shall be used to extend the boring to the desired depth;
- After the hole is made, the hand-auger or slam bar is carefully withdrawn to prevent collapse of the side wall of the boring;

- Connect the soil gas implant to the appropriate length of tubing, and carefully insert the soil gas implant into the borehole to the desired depth;
- Pour clean filter sand into the annular space surrounding the soil gas implant, bringing the sand layer up to at least 2" above the implant;
- Cut the tubing to the desired length, and cap the output end of the tubing using a Swagelok nut, ferrule, and plug; or by connecting a 3-way valve to the sample tubing using silicone tubing.
- Place granular bentonite above the sand pack and hydrate bentonite by adding water,
    - for temporary soil gas monitoring points, the bentonite seal will extend to the surface;
    - for permanent monitoring soil gas monitoring points, the surface seal will be created utilizing quick mix concrete. A PVC cleanout shall be installed above the bentonite seal and cemented into place using the concrete mix.

4 SAMPLING PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sample shall be reported to the Project Manager prior to proceeding with field activities.

Temporary and permanent soil gas monitoring points shall be allowed to equilibrate for 24 hours after installation prior to sampling. Duplicate Samples and potential QC samples shall be collected as required in the specified work plan.

4.1 Summa Canister Sampling

Pace Analytical Laboratories will supply all Summa Canisters, flow controllers, in-line particulate filters, and vacuum gauges. The sampler should inspect the equipment prior to mobilization, to ensure knowledge of assembly. If needed, specific instructions and/or diagrams for system assembly, if any, should be obtained from the laboratory supplying the canister(s). The initial canister vacuum should be verified by the laboratory, prior to shipment, to be approximately -30 inches of mercury (inHg or "Hg). The sampler shall also inspect the canister prior to mobilization to identify any defects and/or loose fittings. The sampler will check the flow rate on the regulator and confirm the appropriate sampling time. Samples will be collected over an 8-hour period.

Sampler shall record the ambient temperature in the field logbook, immediately prior to sample collection.

In general, assembly of the sampling apparatus, sample collection, and documentation shall be performed as follows:

- Confirm that the valve is closed;
- Remove brass cap from the canister;
- Connect the flow controller (if provided separate from the Summa canister assembly), with attached vacuum gauge, to the canister utilizing a compression fitting;
- Using a wrench, ensure brass plug or cap on the intake end of the flow controller is attached and tightened, creating an airtight train, and quickly open and close the canister valve to check for leaks,
    - if the needle on the gauge drops, the train is not airtight – try refitting and/or tightening connections until the needle holds steady,
    - if gauge continues to drop, contact Project Manager for instructions on proceeding,
    - do not over tighten brass caps/plugs;
- Attach the appropriate amount of tubing to the sampling port, needed to reach the sample inlet on the filter/flow controller;
- Prior to sampling, the amount of air in the soil gas monitoring point (i.e., the air within the pore space of the granular backfill, soil gas implant, and associated tubing) should be calculated. This volume should be purged from the monitoring point prior to sampling. In order to purge this volume, the following steps should be employed:
    - Disconnect Swagelok cap/plug from sample port;
    - Attach three way valve to sample port, using additional tubing, if necessary;
    - Attach 60 cc gas-tight syringe to three way valve, using additional tubing if necessary;
    - Turn three way valve so that valve is open to both the sample port and 60 cc gas-tight syringe;
    - Extract purge volume by withdrawing air using the syringe plunger;
    - Turn three way valve so that valve is open to both the syringe and to the outside air, and evacuate syringe; and
    - Repeat until sufficient volume of air is purged.
    - Once a sufficient volume of soil gas has been purged, attach tubing connected to the sampling port to the sample inlet on the filter/flow controller.
- Begin sampling by opening the canister valve as specified by the manufacturer and/or laboratory;
- Record the sample number, location, date, flow controller and canister serial numbers, initial vacuum reading, and start time in the field logbook,
    - the initial canister vacuum should be at least -25 inches of mercury (inHg or ”Hg). If the initial canister vacuum is less than -25 inHg, (i.e., between 0 inHg and -24 inHg), report condition to the Project Manager.
- After sampling is complete, close the canister valve and record the end time and final canister vacuum in the field logbook and disassemble the flow controller/gauge,
    - do not over-tighten the valves or brass caps/plugs (i.e., hand-tighten and ¼ turn with a wrench for caps/plugs),

  - the final canister vacuum should generally be between -3 inHg and -10inHg, and at a minimum be sub-atmospheric;
- Fill out canister sample tag, making sure the sample ID and date of collection recorded on the sample tag matches what is recorded on the chain-of-custody (COC), and affix tag to canister;
- Package the canisters and flow controllers in the laboratory-provided shipping container or box and transport to the laboratory, from which the canisters were rented, under COC protocol.

Sample management; including COC, handling, packing, and shipping procedures shall be in accordance with the procedures and requirements of SOP No. 011 *"Sample Handling, Packing, Shipping and Chain of Custody"*.

4.2 Leak Testing

To ensure that valid soil gas samples are collected, and to provide quantitative proof of the integrity of the surface seal by demonstrating that breakthrough of air from the surface is not occurring, leak tests will be performed prior to sample collection. Leak tests should be conducted once at each implant to check the tightness of the sampling chain (implant, valves, and tubing). Additional sampling from the same implant does not require repeat testing. Leak testing should be conducted after the implant has settled in, allowing the grout to be fully cured. The testing involves the introduction of a gaseous tracer compound (helium) into a shroud which covers the sampling point, and then monitoring with a hand held meter for the presence of helium in the air withdrawn from the subsurface.

While the shroud is inflated, air is purged from the monitoring point using a three-way valve and a syringe. Using the same three-way valve and a syringe, a Tedlar bag is then filled with at least 500 mL of air that is withdrawn from the monitoring point. The air inside of the Tedlar bag is then screened in the field with the meter. If low concentrations of the tracer gas are observed in the Tedlar bag sample, the seal can be considered competent and sampling can continue. If high concentrations of the tracer gas are observed in the Tedlar bag (e.g., >10% of the starting concentration within the shroud), connections in the sampling train are checked, and the test is repeated. If tracer concentrations in the sample line still exceed the threshold of 10%, and there are no other explanations for the detections, the boring or vapor monitoring point should be abandoned, reinstalled and the leak test repeated once again.

4.2.1 Procedure

- Once the soil gas monitoring point has been installed and the borehole sealed, place a small clear garbage bag (the shroud) over the sample location.
- Place the sand filled hose around the edges of the shroud, weighting it down.

- Pass the sample tubing under the edge of the shroud allowing only the end of the tubing to extend outside of the shroud.
- Pass the helium supply line and helium meter tubing under the edge of the shroud.
- Attach the helium cylinder and regulator to the helium supply line.
- Attach a 3-way valve to the sample tubing with silicone tubing.
- Attach the syringe to the 3-way valve.
- Introduce the tracer gas (helium) through the helium supply line and "inflate" the shroud. Continue to add helium as needed to keep the shroud "inflated".
- Use the 3-way valve and syringe to remove three tubing volumes of air; discharging the air to the atmosphere.
- After the three tubing volumes of air have been purged, using the 3-way valve and syringe, fill the Tedlar bag with at least 500 mL of air.
- Close the 3-way valve and attach the helium detector to the Tedlar bag
- Using the meter's internal pump, measure the concentration of helium in the Tedlar bag with the helium meter and record the results.

5 SAMPLING LOCATION ABANDONMENT

Following the collection of any necessary samples, temporary soil gas monitoring points, including those installed via direct push methods shall be abandoned in accordance with the requirements of COMAR 26.04.04.36.

6 SAMPLE ANALYSIS

All air samples will be analyzed for VOCs by EPA Method TO-15. This method uses gas chromatography/mass spectrometry (GC/MS) to identify and quantify target VOCs. The technical holding time for method TO-15 is 14 days from collection.

7 REFERENCES

EPA (1999). *Compendium Method TO-15 – Determination of Volatile Organic Compounds (VOCs) in Ambient Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry.* Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air – 2nd Edition. EPA/625/R-96/010b. Center for Environmental Research Information, Office of Research and Development, United States Environmental Protection Agency. Cincinnati, OH. January, 1999.

ITRC (2007). *Vapor Intrusion Pathway: A Practical Guide.* Interstate Technology and Regulatory Council. Washington D.C.. January, 2007.

KDHE (2007). *Kansas Vapor Intrusion Guidance.* Bureau of Environmental Remediation, Division of Environment, Kansas Department of Health and Environment. Topeka, KS. June, 2007.

OSWER (2015). Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air.

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SOP No. 003
SEDIMENT SAMPLING
STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) identifies the equipment and techniques used in the collection of discrete or composite representative sediment samples. For the purposes of this procedure, sediments are those mineral and organic materials situated beneath an aqueous layer. The aqueous layer may be static, e.g., lakes, ponds, or impoundments, or flowing, as in rivers and streams.

2 EQUIPMENT

The equipment and methods for the collection of sediment samples will vary dependent upon project specific conditions and objectives. Recovery of sediment can be done directly using a hand-held device such as a shovel, trowel, or auger, or indirectly using a remotely activated device such as an Eckman or Ponar dredge. The procedures presented in this SOP identify sediment collection via direct methods and via dredges on-board watercraft. Depending on the method used for collection, the equipment needed may include the following:

- maps/plot plan
- safety equipment
- compass
- tape measure
- survey stakes, flags, or buoys and anchors
- camera and film
- stainless steel buckets
- 4-oz, 8-oz, and 1-quart, wide-mouth jars w/Teflon-lined lids
- Ziploc plastic bags
- field logbook
- sample jar labels
- chain of custody forms
- field data sheets
- cooler(s)
- ice

- decontamination supplies/equipment
- spade or shovel
- spatula
- scoop
- trowel
- bucket auger
- thin-walled auger
- extension rods
- T-handle
- Waders
- sampling trier
- sediment coring device (tubes, points, drive head, drop hammer, "eggshell" check valve devices, acetate cores)
- nylon rope
- Ponar dredge
- boat

3 SAMPLE LOCATIONS

Samples should be collected at or as close as possible to the locations provided in project work plan. Specific site characteristics, including flow regime, basin morphometry, sediment characteristics, depth of overlying aqueous layer, and extent and nature of contamination should be considered when selecting sample location. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

4 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sampler shall be reported to the Project Manager prior to proceeding with field activities.

4.1 Preparation

- Determine the extent of the sampling effort, the sampling methods to be employed, and which equipment and supplies are required;
- Obtain necessary sampling and monitoring equipment;
- Decontaminate or pre-clean equipment, and ensure that it is in good working order;
- Perform a general site survey prior to site entry;

- Use stakes, flags, or buoys to identify and mark all sampling locations.

4.2 Sample Collection

Selection of a sampling device is most often contingent upon: (1) depth of water at the sampling location, and (2) the physical characteristics of the medium to be sampled.

4.2.1 Sampling Surface Sediment with a Thin-Wall Tube Auger from Beneath a Shallow Aqueous Layer

This system consists of an auger, a series of extension rods, and a "T" handle. The auger is driven into the sediment and used to extract a core. A sample of the core is taken from the appropriate depth.

Use the following procedure to collect sediment samples with a thin-walled auger:

- Insert the auger into the material to be sampled at a 0° to 45° angle from vertical. This orientation minimizes spillage of the sample from the sampler. Extraction of samples may require tilting of the sampler.
- Rotate the auger once or twice to cut a core of material.
- Slowly withdraw the auger, making sure that the slot is facing upward.
- An acetate core may be inserted into the auger prior to sampling, if characteristics of the sediments or body of water warrant. By using this technique, an intact core can be extracted.
- Transfer the sample into an appropriate sample or homogenization container.

4.2.2 Sampling Deep Sediments with Augers and Thin-Wall Tube Samplers from Beneath a Shallow Aqueous Layer

This system uses an auger, a series of extension rods, a "T" handle, and a thin-wall tube sampler. The auger bores a hole to a desired sampling depth and then is withdrawn. The auger tip is then replaced with a tube core sampler, lowered down the borehole, and driven into the sediment at the completion depth. The core is then withdrawn and the sample collected. This method can be used to collect consolidated sediments, but is somewhat limited by the depth of the aqueous layer.

Several augers are available which include bucket and posthole augers. Bucket augers are better for direct sample recovery, are fast, and provide a large volume of sample. Posthole augers have limited utility for sample collection, as they are designed more for their ability to cut through fibrous, rooted, swampy areas.

Follow these procedures to collect sediment samples with a hand auger:

- Attach the auger bit to a drill extension rod, then attach the "T" handle to the drill extension rod.

- Clear the area to be sampled of any surface debris.
- Begin augering, periodically removing any accumulated sediment from the auger bucket.
- After reaching the desired depth, slowly and carefully remove the auger from boring. (When sampling directly from the auger, collect sample after the auger is removed from boring and proceed to transfer sample into an appropriate sample or homogenization container.)
- Remove auger tip from drill rods and replace with a precleaned thin-wall tube sampler. Install proper cutting tip.
- Carefully lower tube sampler down borehole. Gradually force tube sampler into sediment. Care should be taken to avoid scraping the borehole sides. Also avoid hammering of the drill rods to facilitate coring, since the vibrations may cause the boring walls to collapse. Remove tube sampler and unscrew drill rods.
- Remove cutting tip and remove core from device.
- Discard top of core (approximately 1 inch), as this represents material collected by the tube sampler before penetration of the layer of concern.
- Transfer sample into an appropriate sample or homogenization container.

4.2.3 Sampling Deep Sediments with Ponar Dredge

Sediment dredges such as Ponar Dredges are utilized when the sediment is not readily obtainable (*i.e.,* at great depths or partially consolidated). The dredge consists of two clamshell-shaped metal buckets operated by a control hinge and line. Dredges should never be allowed to free fall into the substrate, but rather be carefully lowered to minimize dispersal of fine-grained material. If surface water samples are to be collected from the same location, the surface water sample should be collected first to minimize sediment resuspension in the area.

If the use of a boat is required for the collection of a sediment sample (and/or surface water sample), all engines should be turned off and samples should be collected upstream of the engine or other machinery that may release exhaust fumes or fuel into the water.

The "mini" or "petite" Ponar dredge is a smaller, much lighter version of the Ponar dredge. It is used to collect smaller sample volumes when working in industrial tanks, lagoons, ponds, and shallow water bodies. It is a good device to use when collecting sludge and sediment containing hazardous constituents because the size of the dredge makes it more amenable to field cleaning. The "petite" Ponar dredge should be utilized when collecting sediment samples on-board a boat.

Sampling shall be performed starting at the most downstream location and work upstream, to avoid entraining disturbed sediments in the samples. Accordingly, if samples are being collected from a non-flowing water body, sampling shall be performed starting at the most leeward (downwind) location and work windward (upwind), to avoid entraining disturbed sediments in the samples.

The following procedures shall be followed when operating a Ponar Dredge:

- Inspect the sampler to ensure all parts are in good working condition and that the unit is securely fastened to the line on the hoist.
- Attach a sturdy nylon or steel cable to the hook provided on top of the dredge.
- Arrange the Ponar dredge sampler in the open position, setting the trip bar so the sampler remains open when lifted from the top.
- Slowly lower the sampler to a point just above the sediment.
- Lower the sampler slowly. When the line slackens, desired depth has been obtained and the pinch-pin pops out.
- Drop the sampler sharply into the sediment, then pull sharply up on the line, thus releasing the trip bar and closing the dredge.
- Raise the sampler to the surface and slowly decant any free liquid through the screens on top of the dredge. Be careful to retain fine sediments.
- Open the dredge and transfer the sediment to a stainless steel or plastic bucket. Continue to collect additional sediment until sufficient material has been gained. Thoroughly mix sediment to obtain a homogeneous sample, and then transfer to the appropriate sample container.
- Samples for volatile organic analysis must be collected directly from the bucket before mixing the sample to minimize volatilization of contaminants.

Only "successful grabs" (i.e., consisting of complete closure of sampling device jaws and devoid of large quantities of gravel, rocks, sticks, leaves, and detritus) will be retained for analysis. Dredges should be decontaminated between sample locations.

4.2.4 Wet Sediment Sampling

The "suction sampler" is a modified surge block device similar in design concept as a well development system. The suction sampler consists of a 2" diameter PVC pipe and the surge block that includes two 1 7/8 inch diameter washers with a piece of rubber between them attached to a 1-inch PVC pipe. The washers and rubber slide over a threaded PVC fitting and a nut holds them onto the 1-inch pipe. The surge block slides into the 2-inch PVC pipe and the rubber between the washers creates a seal. As the nut is tightened, the rubber is squeezed out from between the washers, which increases the seal.

To collect a sample the apparatus is driven into soft sediment, with the surge block at the bottom of the 2-inch tube, until the required sampling depth is achieved. Once at the desired sampling depth, the apparatus is withdrawn for a foot and lowered back to the bottom while pulling the surge block up through the interior of the 2-inch pipe, creating a vacuum and pulling the sediment into the sampler. The apparatus is then extracted, tilting it as the bottom reaches surface grade. Sample material is then recovered out of the tube into a plastic bag and then distributed as required to sample containers.

4.3 QUALITY ASSURANCE/QUALITY CONTROL

All data must be documented on field data sheets or within field logbooks. All instrumentation shall be operating in accordance with the procedures detailed herein and the manufacturer instructions provided in the instrument-specific operation manual. Operation manuals for sediment sampling instrumentation, anticipated to be used on this project, can be found in Appendix E of the QAPP.

Sample management; including COC, handling, packing, and shipping procedures shall be in accordance with the procedures and requirements of *SOP No. 011 "Sample Handling, Packing, Shipping and Chain of Custody"*.

Equipment calibration activities must occur prior to sampling/operation, and they must be documented in the Field Logbook

Once samples have been placed into the appropriate sample containers, sample ID, sample location, and sample date and time of collection should be recorded on the sample label. This information shall be consistent with what is recorded on the chain-of-custody (COC).

All sample containers will be packed in a cooler on ice or ice packs to maintain the holding temperature of 4 degrees C or less.

Field QC samples should be collected as required per the project work plan or project planning documentation.

5 SAMPLE ANALYSIS

The project specific work plan should be consulted prior to sampling to determine which analytical methods are required and are appropriate to satisfy project data needs. Sediment samples will generally be analyzed for the complete project analyte list for soils provided on Worksheet # 15 of the QAPP; however, certain project tasks will have target analyte lists limited to a subset of the complete list, as detailed in the task specific work plan. Worksheets 19 and 30 of the QAPP shall be consulted for specifications regarding sample containers, preservation, and hold times.

6 REFERENCES

EPA. (1999). *Field Sampling Guidance Document #1215. Sediment Sampling.* USEPA Region 9 Laboratory. Richmond, California.

SOP No. 004
SURFACE WATER SAMPLING
STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) identifies the equipment and techniques used in the collection of liquid samples, both aqueous and non-aqueous, from streams, rivers, lakes, ponds, lagoons, embayments, and surface impoundments. This specific SOP is limited to samples collected at or near the surface utilizing direct methods.

2 EQUIPMENT

The equipment and methods for the collection of surface water samples will vary dependent upon project specific conditions and objectives.

Equipment needed for the collection of surface water samples may include:

- Water Quality Multi-meter (for the measurement of temperature, pH, dissolved oxygen, conductivity, oxidation-reduction potential (ORP), and, if necessary, turbidity)
    - Stand-alone turbidity meter may be required.
- Dip sampler
- Sample collection bottles
- Sample bottle preservatives
- Ziploc bags
- Ice
- Cooler(s)
- Chain-of-Custody forms (COCs)
- Field data sheets
- Decontamination equipment
- Maps/plot plan
- Safety equipment
- Gloves
- Waders
- Compass
- Tape measure

- Survey stakes, flags, or buoys and anchors
- Camera
- Boat
- Waterproof pen
- Sample bottle labels
- Field Logbook

3 SAMPLE LOCATIONS

Samples should be collected at or as close as possible to the locations and depths provided in project work plan. In order to collect a representative sample, the hydrology and morphometrics (e.g., measurements of volume, depth, etc.) of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons or impoundments, flow patterns in streams, and appropriate sample locations and depths.

If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

4 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sampler shall be reported to the Project Manager prior to proceeding with field activities.

4.1 Preparation

- Determine the extent of the sampling effort, the sampling methods to be employed, and which equipment and supplies are required;
- Obtain necessary sampling and monitoring equipment;
- Decontaminate or pre-clean equipment, and ensure that it is in good working order;
- Perform a general site survey prior to site entry;
- Use stakes, flags, or buoys to identify and mark all sampling locations.

Generally, the deciding factors in the selection of a sampling device for sampling liquids in streams, rivers, lakes, ponds, lagoons, and surface impoundments are:

- Will the sample be collected from the shore, in-stream, or from a boat on the impoundment?
- What is the overall depth and flow direction of river or stream?

- What is the chemical nature of the analyte(s) of concern? Do they float on the water surface (collect by skimming the surface) or are they miscible (soluble) and are more likely to be present at depths (collect sub-surface)?

4.1.1 Sampler Composition

The appropriate sampling device must be of a proper composition. Only glass sample collection containers shall be used for this project.

4.2 Sample Collection

Regardless of the method employed to collect a surface water sample, unless there is reason to believe that potential contaminants would be localized at the water surface (such as the presence of a sheen or floating product on the surface), surface water samples should be collected from mid-depth in the water column. Measurements of temperature, pH, conductivity, dissolved oxygen, turbidity, and oxygen-reduction potential (ORP) shall be made at the sampling location prior to collection of a sample into the appropriate sample container. A sample of surface water shall be collected using a glass collection container and transferred to the measurement container of the multi-parameter meter and/or turbidity meter. The values of these measurements shall be recorded in the Field Logbook.

4.2.1 Dip Sampler

A dip sampler is useful for situations where a sample is to be recovered from an outfall pipe or along a lagoon bank where direct access is limited. The long handle on such a device allows access from a discrete location. Sampling procedures can be found in Appendix E of the QAPP and are as follows:

- Assemble the device in accordance with the manufacturer's instructions;
- Extend the device to the sample location and collect the sample; and
- Retrieve the sampler and transfer the sample to the appropriate sample container.

4.2.2 Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect water samples. This method is not to be used for sampling lagoons or other impoundments where contact with contaminants are a concern.

Using adequate protective clothing, access the sampling station by appropriate means. The use of waders to access the surface water, especially for non-flowing water bodies, should be avoided unless other options cannot be used due to site conditions, as the disturbance of the sediment may impact the surface water sample. For shallow stream stations, the sampler should face upstream and collect the sample without disturbing the sediment. Surface water samples should always be collected prior to a sediment sample at the same location. The collector submerses the closed sample

container, opens the bottle to collect the sample and then caps the bottle while sub-surface. The collection bottle may be rinsed two times by the sample water. For lakes and other impoundments, collect the sample under the water surface avoiding surface debris and the boat wake.

When using the direct method, do not use pre-preserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation.

4.2.3 Sampling with the Assistance of a Boat

If using a boat, all engines should be turned off and samples should be collected upstream of the engine or other machinery that may release exhaust fumes or fuel into the water.

If sediment samples are to be collected from the same location, the surface water sample should be collected first to minimize sediment resuspension in the area.

Sampling shall be performed starting at the most downstream location and work upstream, to avoid entraining disturbed sediments in the samples. Accordingly, if samples are being collected from a non-flowing water body, sampling shall be performed starting at the most leeward (downwind) location and work windward (upwind), to avoid entraining disturbed sediments in the samples.

4.3 QUALITY ASSURANCE/QUALITY CONTROL

All data must be documented on field data sheets or within field logbooks. All instrumentation shall be operating in accordance with the procedures detailed herein and the manufacturer instructions provided in the instrument-specific operation manual. Operation manuals for surface water sampling instrumentation, anticipated to be used on this project, can be found in Appendix E of the QAPP.

Equipment calibration activities must occur prior to sampling/operation, and they must be documented in the Field Logbook.

Sample management; including COC, handling, packing, and shipping procedures shall be in accordance with the procedures and requirements of *SOP No. 011 "Sample Handling, Packing, Shipping and Chain of Custody"*.

Once samples have been placed into the appropriate sample containers, sample ID, sample location, and sample date and time of collection should be recorded on the sample label. This information shall be consistent with what is recorded on the chain-of-custody (COC).

All sample containers will be packed in a cooler on ice or ice packs to maintain the holding temperature of 4 degrees C or less.

Field QC samples should be collected as required per the project work plan or project planning documentation.

5 SAMPLE ANALYSIS

The project specific work plan should be consulted prior to sampling to determine which analytical methods are required and are appropriate to satisfy project data needs. Surface water samples will generally be analyzed for the complete project analyte list for groundwater provided on Worksheet # 15 of the QAPP; however, certain project tasks will have target analyte lists limited to a subset of the complete list, as detailed in the task specific work plan. Worksheets 19 and 30 of the QAPP shall be consulted for specifications regarding sample containers, preservation, and hold times.

SOP No. 005
INVESTIGATION-DERIVED WASTES MANAGEMENT
STANDARD OPERATING PROCEDURE
Rev. 02

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1 SCOPE

This Standard Operating Procedure (SOP) identifies the general guidelines for the management of investigation-derived wastes (IDW). The anticipated IDW that will be generated includes, but is not limited to:

- Drill cuttings and Drilling fluids generated from soil borings or wells installations;
- Groundwater generated during well development, monitoring well purging, aquifer testing, remedial activities, or other operations;
- Light Non-Aqueous Phase Liquids (LNAPL) and Dense Non-Aqueous Phase Liquids (DNAPL);
- Waste water and sediment generated during equipment decontamination procedures;
- Used personal protective equipment (PPE); and
- Miscellaneous debris.

2 EQUIPMENT

IDW Management requires limited equipment. The following should be available on-site:

- Clean, new 55-gallon drums with lids;
- Socket and/or adjustable wrenches
- PPE
- Grease pen, paint, or paint stick for labeling
- Labels to indicate drum contents, media, and origin
- Plastic sheeting (if necessary)
- Spill containment berms (if necessary)
- Caution tape

3 PROCEDURES

3.1 Containerization

- All potentially impacted materials generated during any investigation or remedial activity must be containerized unless one of the exceptions described below under Item 10 apply. Unless directed otherwise by the client, containers (drums, frac tanks, roll-off boxes, etc.) are to be provided by the consultant or contractor.
- All potentially impacted materials shall be placed in new or reconditioned 55-gallon (DOT-UN1A2) drums. All drums brought onsite must be clean and in sound condition, free of any rust, dents, holes, or other types of damage.
- Various types of waste materials (e.g., soils, groundwater, PPE, etc.) must be containerized separately without exception. Additionally, dry and wet soils should be containerized separately, if feasible.
- Materials generated from various plant process areas, which may require potentially different waste classifications, should be containerized separately. As an example, soils generated in the vicinity of a surface impoundment which managed sludge from the treatment of wastewater from wood treating operations that use creosote and/or pentachlorophenol (EPA Hazardous Waste K001) should be containerized separately from soils generated in a creosote drip track area (EPA Hazardous Waste F034). Likewise, materials generated at off-site locations should be managed separately from those generated on-site.
- If possible, drums should be filled to approximately 90% capacity. As necessary, drums containing liquids should have enough freeboard to prevent rupture in the event of freezing.
- Containers inside of containers are not permitted by waste management regulations. As a result, PPE must be placed directly into the drum. **Do not place PPE in a plastic bag and in turn place the plastic bag into a drum.** This constitutes a violation of waste management regulations. Similarly, all soil samples must be removed from jars or plastic bags and the jars crushed or plastic bags torn prior to being placed in a drum.
- All lids and gaskets must be securely fastened prior to moving from one location to another. The consultant or subcontractor is responsible for transporting containers to an on-site temporary staging area as directed by the Facility Waste Management Director. Containers must be loaded, transported and unloaded in a safe manner.
- The exterior of all containers must be thoroughly cleaned prior to staging. All mud, dirt or debris must be removed, with no exception. Waste management facilities will not accept containers which are visibly dirty on the outside.
- Under no circumstances shall non-waste materials or general trash be placed in waste containers. The consultant/subcontractor should provide a dumpster for management of non-waste materials and general trash.
- Pending analysis, all groundwater and/or decontamination liquids may discharged into the on-site treatment system in accordance with the existing discharge permit.

3.2 Container Designation and Labeling

- Each container will be assigned a unique designation. This designation should include a sequential number associated with each waste type, a code which identifies the type of waste (e.g., "S" for soil, "GW" for groundwater, etc.), and the date the material was placed in the container (e.g. 1-GW-12/12/15; 2-GW-12/12/15 etc...). The container designation must be clearly marked on the lid and the side of the container prior to transport to the temporary on-site staging area. The markings must be made in a manner such that the markings are legible, highly visible and permanent (i.e., weather resistant). A "Mean Streak®" grease pen or a paint stick is recommended for marking the container.
- A "Non-Hazardous Waste" label shall initially be affixed to the exterior side of the drum at a location at least two-thirds of the way up from the bottom of the container. Under the optional information section on the label, the following statement may be included "Material Classification Pending Results of Analysis".
- If IDW is known to be hazardous, the following information shall be placed on all "Hazardous Waste" labels and affixed to the container:
    - Description of contents (i.e., purge water, soil cuttings);
    - Characteristics of waste (i.e. waste code or hazard class);
    - Generator information (i.e., name, address, contact telephone number);
    - EPA identification number (supplied by on-site client representative);
    - Date when the waste was first accumulated.
- The following information is to be recorded by field personnel in the field logbook, as necessary:
    - Container Designation;
    - Contents;
    - Date that the container was filled;
    - Location where the drums are staged;
    - Location where the material was generated;
    - Relative moisture content for soils, e.g., dry, moist, wet, saturated;
    - Approximate volume or percentage of the container filled.

3.3 Container Storage

- All containers are to be transported to an on-site staging area, all container handling and moving must be conducted in a safe manner. Contractors are responsible for providing the necessary equipment (e.g., front-end loader, fork lift with drum grappler, etc.) to provide for safe and efficient staging of containers. **Figure 1** shows the location of the on-site IDW accumulation and staging area.

- All containers shall be stored in a neat and organized fashion with all labels clearly visible. Containers shall not be stacked.
- Containers holding materials of different waste classifications should be staged together to facilitate loading of the materials onto transport vehicles.
- To the extent practicable, all containers should be protected from the elements.
- If stored outdoors in an area where precipitation could accumulate, all containers must be placed on pallets.
- In accordance with DOT requirements, all containers must be rust-free and in sound condition for shipment.
- Prior to demobilization, field personnel should conduct an inspection of the container storage area to ensure all containers are clearly marked, clean and staged in a neat and organized manner.

A section of the on-site staging area shall be secured and designated as the "hazardous waste storage area". The following requirements for the hazardous waste storage area must be implemented:

- Proper hazardous waste signs shall be posted;
- Secondary containment to contain spills;
- Spill containment equipment must be available;
- Fire extinguisher;
- Adequate aisle space for unobstructed movement of personnel.

3.4 Waste Material Inventory

An inventory of IDW, stored at the project site, should be maintained in the field logbook and entered in to the Project File following demobilization at the site. Hazardous IDW may be stored in the on-site staging area for a maximum of 90 days before it must be manifested and shipped to the designated facility provided in Section 3.6 (below). MDE will be notified within 24 hours of any hazardous waste determination and the date this material entered the IDW accumulation and staging area. Information contained in the IDW inventory should include the following:

- Activity or project phase related to waste generation;
- Type of container;
- Container designation;
- Container contents;
- Generation date;
- Staged location;
- Location where IDW was generated;
- Relative moisture content for soils;
- Volume or percentage contained;

- Comments; and
- Date removed.

3.5 Waste Material Sampling and Analysis

Composite samples of the containerized materials for laboratory analysis may be collected for each IDW media. The results of the analysis may be used for waste profiling purposes required by the waste management facility and/or waste classification purposes. To the extent practicable, historical information, site-specific analytical data and knowledge of the waste composition should be utilized to minimize sampling and analysis requirements.

- Specific details regarding the number and types of samples to be collected, required laboratory turn-around time, analytical parameters and analytical methods will be determined on a project-specific basis during the initial planning phase. If applicable, this information may be presented in a project-specific waste management plan.
- At a minimum, samples must be collected and handled in accordance with standard industry protocols. If an approved project-specific Sampling and Analysis Plan or Quality Assurance Project Plan exists, then sample collection and handling procedures, as specified therein, must be followed.
- All analyses must be performed using the appropriate analytical methods specified in EPA SW846 "Test Methods for the Evaluation of Solid Wastes".
- The sampler must complete and maintain copies of all chain-of-custody documentation.
- In accordance with Subpart CC or 40CFR Par 264/265 which became effective on December 6, 1996, hazardous wastes containing greater than 500 parts per million by weight total volatile organic compounds (VOCs), are subject to the emission control requirements of this rule. Determination of VOC content may be made through laboratory analyses or generator knowledge. Thus, analysis for VOCs will likely be required by the waste disposal facility for profiling purposes in the future. Analysis is to be performed using method 25D in 40CFR Part 60 Appendix A, or through the use of an approved alternate method. Knowledge-based waste determinations must be thoroughly documented.
- Composite samples of similar waste classification of containerized materials will be profiled based on the characteristics presented in 40 CFR Part 261 Subpart C - Characteristics of Hazardous Wastes:
    - §261.21 – Characteristic of Ignitability
    - §261.22 – Characteristic of Corrosivity
    - §261.23 – Characteristic of Reactivity
    - §261.24 – Toxicity Characteristic
- All laboratory analysis for waste characterization must be performed within 45 days of the generation date.

3.6 Transportation and Disposal

All hazardous and most non-hazardous IDW will be transported off-site by Clean Venture or Clean Harbors to a permitted treatment and disposal facility. Non-hazardous drill cutting may be disposed of on-site at the Greys Landfill.

All analytical results, disposal facilities and volumes and type of IDW generated for each Parcel will be provided to MDE prior to transport off-site.

Contact:
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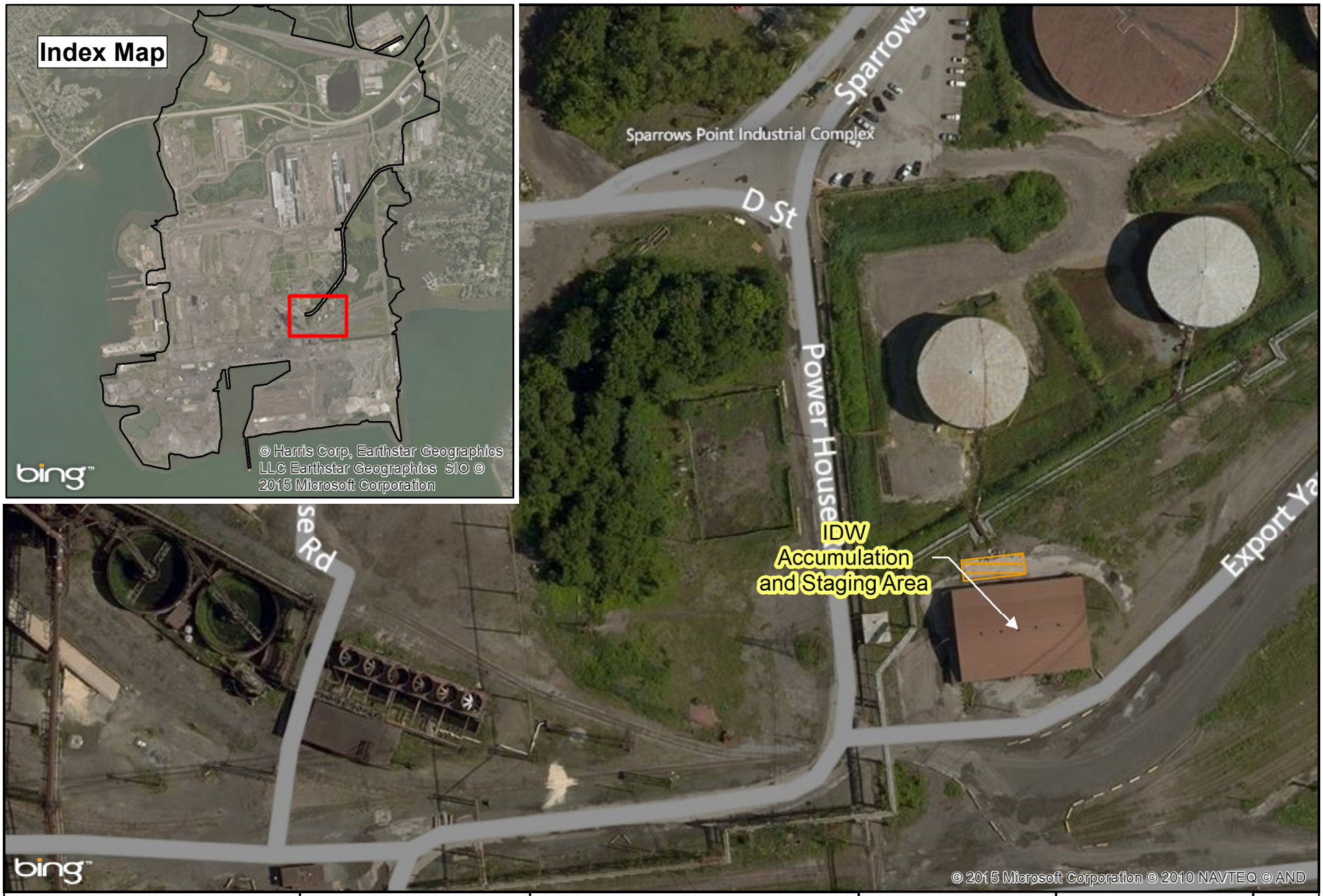


ARM Group Inc.
Earth Resource Engineers and Consultants

0 35 70 140 Feet

SOP No. 5 - Investigation-Derived Wastes (IDW) Accumulation and Staging Area

September 1, 2015

EnviroAnalytics Group	Sparrows Point Terminal
ARM Project 150241M	Baltimore County, MD

Figure 1

SOP No. 006
GROUNDWATER SAMPLING
STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

This Standard Operating Procedure (SOP) identifies the general guidelines for the collection of groundwater samples from monitoring wells, piezometers (including those installed via direct push borings), and extractions wells. Groundwater samples are collected to gather information regarding inorganic and organic constituents in the groundwater, as well as water quality or natural attenuation indicator parameters. This SOP discusses and is limited to the procedures utilized for the physical collection of groundwater samples.

Effort must be made to ensure that the sample collected is representative of the particular zone being sampled.

Due the numerous methods and equipment that may be employed in the collection of groundwater samples, this SOP should be used in conjunction with project-specific documentation, i.e., work plans or sampling and analysis plans.

Low-flow sampling is preferred for groundwater sample collection. In certain instances, however, complete low-flow methodology may not be able to be employed (e.g., small diameter temporary piezometers). Specific low-flow sampling techniques are provided in SOP#007.

2 EQUIPMENT

Groundwater sampling may require a significant amount of equipment and materials. In general, purging and sample collection from a monitoring point can be achieved by the use of a pump or bailer. The type of pump or bailer utilized will depend on the characteristics of the well and aquifer, data quality objectives, availability of a power source, and often, which suite of parameters are being analyzed from the sample. Regardless of sampling methods, the following equipment should be mobilized at the site prior to sample collection, unless otherwise specified in project-specific documentation:

- Water Quality Multi-meter (for the measurement of temperature, pH, dissolved oxygen, conductivity, oxidation-reduction potential (ORP), and, if necessary, turbidity)
- Tubing of appropriate material for groundwater discharge
- Filtration apparatus (as needed)

- Water-level meter or depth sounder, and NAPL-level meter
- Field logbook
- Sampling/Purge sheets
- Distilled Water
- Sample containers
- Sample labels
- Indelible ink pen
- Decon materials
- 5-gallon buckets
- Twine
- PPE
- Chain-of-Custody forms (COCs)
- Coolers
- Paper Towels
- Garbage bags
- Nitrile or Latex Gloves
- Eye Protection
- Measuring Cup
- Stopwatch
- Tape
- Calibration Solutions
- Bailers
- External Power Source
- First Aid Kit
- Stop Watch
- Calculator
- Well lock key(s)

A number of pump types may be used for the collection of groundwater samples, each having inherent advantages/disadvantages. If pumps are used in groundwater sampling, the type of pump should be specified in project plan, including dedicated pumps present in the sampling monitoring points. The following presents a list of various pump types that may be used in groundwater sample collection:

- Suction Lift Pumps
    - Limited to shallow depths to water.
    - Readily available, portable, and inexpensive.
    - May cause unrepresentative volatilization of low-levels of Volatile Organic Compounds (VOCs).

- Portable Submersible Pumps
    - May be used to sample several monitoring wells in a brief period of time.
    - Relatively large pumping rates can be accommodated.
    - May be limited by size of well casing.
- Air Lift Pumps
    - Portable and light weight.
    - Can handle very deep depths to water.
    - Capable of producing very high flow rates.
    - Air contacts sample causing volatilization.
        - Not recommended for sampling of organic parameters
        - Not recommended for pH sensitive parameters
    - Requires compressed air tank or air compressor.
- Bladder pumps
    - Portable and light weight.
    - Drive gas does not touch sample.
        - Acceptable for all groundwater analyses
    - Slow pumping rate.
    - Requires compressed air tank or air compressor.

Bailers of various materials (materials should be inert or not cause interference with target parameters) are commercially available at various lengths and diameters. Bailers may be top filling or bottom draining. If bailers are to be used, the appropriate bailer type should be specified in the project-specific documentation.

3 SAMPLE LOCATIONS

Sample locations shall be specified in the project-specific documentation, if temporary points (or direct push points) are to be located in the field, these locations shall be located as close as possible to those specified in the approved work plan.

Effort should be made to ensure that the collected sample is representative of the particular zone or depths being targeted.

4 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sample shall be reported to the Project Manager prior to proceeding with field activities.

Several methods or combination of methods may be used to collect groundwater samples from monitoring wells. The chosen methodology(ies) will depend on the parameters to be analyzed, depth of the well, diameter of the well, depth to groundwater, and the required volume of water. Where practical, dedicated or disposable equipment should be used for purging and sample collection to reduce field decontamination requirements and minimize the potential for cross contamination of samples.

Several tasks need to be completed prior to actual sampling of each well. These activities are summarized as follows:

- Check that the proper sample bottles have been received from the laboratory;
- Decontaminate any non-dedicated equipment prior to sampling;
- Measure the static water level prior to purging. Water levels should be measured to nearest 0.01 foot and recorded. If water levels will be used to determine groundwater flow or hydraulic gradients, all measurements should be taken on the same work day over as short a period of time as possible. A record of the static water level shall be maintained on the sampling logs and the Field Logbook;
- The ground surface around the well shall be covered with plastic sheeting.

4.1 Equipment Calibration

Equipment Calibration shall be performed in accordance with the procedures and requirements defined in SOP No. 017 *"Calibration of Field Instruments"*. Records of equipment calibration shall be maintained in the Field Logbook.

4.2 Well Purging

Wells will be purged until at least three casing volumes of water are removed from each well or until the stabilization criteria, as follows, are met:

- pH: ± 0.1 s.u.
- Specific Conductance/Conductivity : ± 3%
- Oxidation-Reduction Potential: ± 10 millivolts
- Turbidity: ± 10% or less than 5 NTU
- Dissolved Oxygen: ± 0.3 mg/L

Measurements should be taken every three to five minutes and recorded on the groundwater sampling/purge log for the low flow sampling method. For the casing volume approach, measure and record the six field parameters after each casing volume is removed from the well. Stabilization is achieved after all parameters have stabilized for three successive readings. In addition, temperature readings shall be recorded along with the aforementioned stabilization parameters.

In order to calculate the volume of water in a well (well volume), the inner casing diameter, total depth of the well, and depth to water must be known or measured. The well volume can be calculated as follows:

Well Volume, V (gal) = π x **well radius** x (**well depth – depth to water**) x **7.48**,

Where:

Well depth, well radius, and depth to water are in feet, and
7.48 is the factor to convert ft^3 to gallons.

If a well is purged dry prior to removal of three well volumes or stabilization, purging is considered complete. Groundwater samples will be collected once a sufficient volume of groundwater has accumulated in the well to completely fill the necessary sample containers. To verify the removal of the required well volumes during purging, a graduated bucket will be used to measure purge water quantities.

Measure the necessary purge volumes by pumping or bailing into a graduated bucket. If the purged water contains a nonaqueous phase (free product) or it is required by the sampling plan, the graduated bucket should be intermittently emptied into a larger storage container (see SOP #005 *Investigation-Derived Waste Management*). If possible, this purge water can be delivered to an onsite treatment system. If an onsite treatment system is not available, options for management of the purge water will be based upon the results of analyses. If no free product is present and the water is not a hazardous waste, the purged water may be disposed of on the ground, away from the top of the well, and in the downgradient direction. If sufficient water is not present for purging of the required volumes, the well should be bailed or pumped dry and permitted to recharge prior to sampling. The time required for purging should be recorded in the field notes and on the Groundwater Well Purge Sheet.

4.3 Sample Collection

After water level recovery, the well should be sampled within 24 hours of completion of the purge event. Dedicated or decontaminated equipment should be used to collect each sample; if practical, low-flow or low-stress sampling techniques should be used (see SOP # 007). If a flow-thru cell was used for the measurement of stabilization parameters, this should be removed prior to sampling. The sampling technician should wear a clean pair of surgical gloves for each well. Samples will be collected in decreasing order of their volatility. This order is generally as follows:

- Volatile Organic Compounds (VOCs)
- Total Organic Halides (TOX)
- Total Organic Carbon (TOC)
- Semi-Volatile Organic Compounds (SVOCs)

- Pesticides and Polychlorinated Biphenyls (PCBs)
- Metals
- Total Phenols
- Cyanide
- Other inorganic parametes, e.g., chloride, nitrate, sulfide, et cetera
- Radionuclides

Samples collected for volatile organics should be carefully placed into 40 ml glass vials with Teflon® septum lids. No air bubbles should be present in the vial after sealing the septum lid; if air bubbles are present, the sampler will collect a new sample to replace the corrupted sample vial. Other common laboratory-provided sample bottles include polyethylene or clear glass for metals and amber glass for phenols and semi-volatiles.

In situations where analysis of dissolved metals is required, field filtration of each sample will be necessary.

After filtering, samples requiring preservatives are preserved and all containers are securely placed in coolers and chilled to an appropriate temperature (usually < 4°C). Each cooler containing samples will contain a completed chain-of-custody form or tag.

4.3.1 Field-filtering for dissolved metals

Groundwater samples collected for dissolved metals analyses will be filtered prior to placement in sample containers. Groundwater sample filtration will be performed using a 0.45 micron, in-line water filter which will minimize contact with air.

Filters should be pre-rinsed with groundwater to ensure the filter media has equilibrated to the sample (following manufacturer recommendations, or passing through a minimum 1 liter of groundwater prior to collecting the sample).

When sampling via bailers, filtering is performed using peristaltic pumps with disposable funnels/filters. New silicone tubing is used in the pump head for each sample filtered and new Teflon tubing is used from the pump head to the filter.

When sampling via pumps, the filtration of groundwater samples shall be performed either directly from the monitoring well or from intermediate sample containers. Groundwater shall then be filtered and discharged from the filtration apparatus directly into sample containers.

All aqueous samples collected for metals analyses must be acidified to a pH of < 2 using trace metal grade nitric acid and cooled to a temperature of ≤ 6°C. In addition, all dissolved metal samples must be filtered within 15 minutes.

5 QUALITY ASSURANCE/QUALITY CONTROL

All data must be documented on field data sheets or within field logbooks. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Instrument and equipment manuals can be found in Appendix E of the QAPP.

Equipment calibration activities must occur prior to sampling/operation, and they must be documented in the Field Logbook.

Sample management; including COC, handling, packing, and shipping procedures shall be in accordance with the procedures and requirements of *SOP No. 011 "Sample Handling, Packing, Shipping and Chain of Custody"*.

Once samples have been placed into the appropriate sample containers, sample ID, sample location, and sample date and time of collection should be recorded on the sample label. This information shall be consistent with what is recorded on the chain-of-custody (COC).

All sample container(s) will be packed in a cooler on ice or ice packs to maintain the holding temperature of 4 degrees C or less.

Field QC samples should be collected as required per the project work plan or project planning documentation.

6 SAMPLE ANALYSIS

The project specific work plan should be consulted prior to sampling to determine which analytical methods are required and are appropriate to satisfy project data needs. Groundwater samples will generally be analyzed for the complete project analyte list for groundwater provided on Worksheet # 15 of the QAPP; however, certain project tasks will have target analyte lists limited to a subset of the complete list, as detailed in the task specific work plan. Worksheets 19 and 30 of the QAPP shall be consulted for specifications regarding sample containers, preservation, and hold times.

SOP No. 007
LOW-FLOW (MINIMAL DRAWDOWN) GROUNDWATER SAMPLING STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

This Standard Operating Procedure (SOP) identifies the general guidelines for the collection of groundwater samples from monitoring wells, piezometers (including those installed via direct push borings), and extractions wells using low-flow or minimal drawdown techniques. Groundwater samples are collected to gather information regarding inorganic and organic constituents in the groundwater, as well as water quality parameters.

Low-flow purging and sampling has the advantages of minimizing the turbidity and mixing between the overlying stagnant casting water and water within the screened interval. Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used; however, this is dependent on site-specific hydrogeology.

2 EQUIPMENT

See SOP No. 006 *"Groundwater Sampling"*

Purging and sampling shall be performed using pumps with a low-flow capability. Peristaltic pumps should be used with caution when samples are collected for volatile organic analyses. Peristaltic pumps can be used when depth to groundwater is less than 20 feet from the ground surface per the Environmental Protection Agency guidance "*Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers*" dated May 2002.

3 SAMPLE LOCATIONS

See SOP No. 006 *"Groundwater Sampling"*

4 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sample shall be reported to the Project Manager prior to proceeding with field activities.

Several tasks need to be completed prior to actual sampling of each well. These activities are summarized as follows:

- Check that the proper sample bottles have been received from the laboratory;
- Decontaminate any non-dedicated equipment prior to sampling;
- Measure the static water level prior to purging. Water levels should be measured to nearest 0.01 foot and recorded. If water levels will be used to determine groundwater flow or hydraulic gradients, all measurements should be taken on the same work day over as short a period of time as possible.
- Unless otherwise specified in project specific documentation, well depths shall be obtained from well logs, rather than sounding prior to collection, as this activity may disturb material settled at the bottom of the well screen.
- The ground surface around the well shall be covered with plastic sheeting.

4.1 Equipment Calibration

Equipment Calibration shall be performed in accordance with the procedures and requirements defined in SOP No. 017 *"Calibration of Field Instruments"*. Records of equipment calibration shall be maintained in the Field Logbook.

4.2 Well Purging

For low-flow, minimal drawdown sampling protocols, an in-line water quality measurement device such as a flow-through cell is used to establish the stabilization time on a well-specific basis for several indicator parameters, as follows:

- pH: ± 0.1 s.u.
- Specific Conductance/Conductivity : ± 3%
- Oxidation-Reduction Potential: ± 10 millivolts
- Turbidity: ± 10% or less than 5 NTU
- Dissolved Oxygen: ± 0.3 mg/L

Measurements should be taken every three to five minutes and recorded on the groundwater sampling/purge log. Stabilization is achieved after all parameters have stabilized for three successive

readings. In addition, temperature readings shall be recorded along with the aforementioned stabilization parameters.

Parameters will typically stabilize in the following order: pH, temperature, and specific conductance, followed by ORP, dissolved oxygen, and turbidity. If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. Note that natural turbidity levels in groundwater may exceed 10 nephelometric units (NTU). Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well.

Performance criteria for determining stabilization should be based on water-level drawdown, pumping rate, and specifications for indicator parameters. Check the water level periodically during purging and sampling to monitor drawdown in the well as a guide to any necessary flow rate adjustment. The goal is minimal drawdown (<0.1 meter) during purging. This goal may not be possible to achieve under some circumstances and may require adjustment based on site specific conditions and personal experience.

4.3 Sample Collection

Once parameters have stabilized, begin sample collection as soon as possible. Disconnect or bypass the in-line monitoring device that was used to measure field parameters prior to sample collection. The sampling flow rate should remain at the established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates <0.5 liters/minute are appropriate. The same device used for purging should be used for sampling.

Samples will be collected in decreasing order of their volatility. This order is generally as follows:

- Volatile Organic Compounds (VOCs)
- Total Organic Halides (TOX)
- Gas sensitive parameters (e.g., Fe^{2+}, CH_4, H_2S/HS^-, alkalinity)
- Total Organic Carbon (TOC)
- Semi-Volatile Organic Compounds (SVOCs)
- Pesticides and Polychlorinated Biphenyls (PCBs)
- Metals
- Total Phenols
- Cyanide
- Other inorganic parameters, e.g., chloride, nitrate, sulfide, et cetera
- Radionuclides

If filtered samples are to be collected, these should be collected last.

Samples collected for volatile organics should be carefully placed into 40 ml glass vials with Teflon® septum lids. No air bubbles should be present in the vial after sealing the septum lid. Extra laboratory provided pre-preserved vials shall be available for the sampler. In the instance that an air bubble is present after sealing the septum lid of the initial sample, the sampler shall collect a new sample to replace the corrupted sample vial.

Sample containers required for the groundwater analytes are presented in QAPP worksheets #19 and # 30.

In situations where analysis of dissolved metals is required, field filtration of each sample will be necessary.

After filtering, samples requiring preservatives are preserved and all containers are securely placed in coolers and chilled to an appropriate temperature (usually < 4°C). Each cooler containing samples; will contain a completed chain-of-custody form or tag.

4.3.1 Field-filtering for dissolved metals

Groundwater samples collected for dissolved metals analyses will be filtered prior to placement in sample containers. Groundwater sample filtration will be performed using a 0.45 micron, in-line water filter which will minimize contact with air.

Filters should be pre-rinsed with groundwater to ensure the filter media has equilibrated to the sample (following manufacturer recommendations, or passing through a minimum 1 liter of groundwater prior to collecting the sample).

When sampling via pumps, the filtration of groundwater samples shall be performed either directly from the monitoring well or from intermediate sample containers. Groundwater shall then be filtered and discharged from the filtration apparatus directly into sample containers.

All aqueous samples collected for metals analyses must be acidified to a pH of < 2 using trace metal grade nitric acid and cooled to a temperature of ≤ 6°C. In addition, all dissolved metal samples must be filtered within 15 minutes.

5 QUALITY ASSURANCE/QUALITY CONTROL

See SOP No. 006 *"Groundwater Sampling"*

6 SAMPLE ANALYSIS

See SOP No. 006 *"Groundwater Sampling"*

SOP No. 008
SURFACE SOIL SAMPLE COLLECTION STANDARD OPERATING PROCEDURE
Rev. 05

1 SCOPE

This Standard Operating Procedure (SOP) describes the procedures for the collection of representative soil samples at the or below the soil surface that can be obtained via the use of hand tools. For this project, surface soil will be considered to be the material at the surface of the site from a depth of 0-12 inches below ground surface. However, if clean surface cover materials, such as paving or gravel, are present, the first one foot of fine-grained material beneath this layer will be collected as surface soil. If initial data indicate a potential for significant lead contamination, then surface soil samples for lead analysis will be collected from the top one inch.

Data derived from surface soil sampling and analysis can be used to address various objectives, including, but not limited to, the following:

1. To support determination of whether a release of constituent(s) of interest has occurred in a specific area.

2. To delineate the nature and lateral extent of a release to support ecological or human health risk assessments via direct contact pathways.

3. To provide information to support modeling exercises such as erosion and runoff estimation or atmospheric transport of dust for risk assessment purposes.

4. To establish background concentrations of naturally-occurring constituents (i.e., metals) in surficial soils.

5. To provide information for establishing site- and task-specific health and safety requirements and for preparation of a Health and Safety Plan.

6. To accommodate area and volume estimation to support cost analysis for viable remedial options.

7. To support remedial design of excavation, in-situ treatment, or engineering control options.

8. To provide an initial data set for the purposes of determining if additional data collection is necessary to identify subsurface soil and groundwater impacts.

2 EQUIPMENT

Equipment may vary depending on specific project objectives. The following is a list of equipment that should, at a minimum, be present for the collection of soil samples near or at the surface:

- Project Work Plan or Sampling and Analysis Plan;
- Indelible ink pens or markers;
- Field Logbook;
- Camera;
- Stainless-steel, glass, or plastic bowls;
- Sample containers;
- Chain-of-custody (COC) forms, custody seals, sample labels;
- Ziploc® bags;
- Insulated cooler;
- Ice;
- Disposable gloves;
- Personal Protective Equipment (PPE);
- Decontamination equipment;
- Hand-held GPS unit;
- Photoionization detector (PID);
- Rubber Mallet;
- Canvas or plastic sheet; and
- Survey stakes or flags.

Surface Soil Sampling:

- Stainless-steel shovel or spade;
- Stainless-steel and plastic spoons;

Auger Sampling

- Stainless-steel bucket auger;
- Auger extension rods;
- Auger handle; and
- Wrenches.

3 LOCATIONS

Soil sample locations shall be collected at or as close as possible to the locations and depths provided in project work plan. Locations shall be confirmed via the use of a hand-held GPS unit prior to sample collection. Otherwise, sample locations shall be staked by a licensed surveyor prior to mobilization.

If required, the proposed locations may be adjusted in the field, based on site access, property boundaries, and surface obstructions. Sample locations where refusal is encountered prior to reaching target depths shall be relocated as close as reasonably possible to the original sample location, unless otherwise directed by the project manager. The sample location (and depth) shall be recorded in the field log book. Where augering is conducted, the location of the boring shall be recorded on the boring log via the use of a hand-held GPS unit or with survey coordinates, where available. The project manager shall be notified if a representative boring cannot be located near the locations provided in the project work plan.

4 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sample shall be reported to the Project Manager prior to proceeding with field activities.

Field personnel shall conduct the following prior to mobilization to the field:

- Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required;
- Ensure all equipment is in working order;
- Decontaminate and pre-clean equipment, as necessary; and
- If subsurface sampling is to be performed, utility clearances shall be performed as described in the following section.

4.1 Utility Clearance

Underground utility locating will be conducted prior to all subsurface exploration greater than one (1) foot in depth. All public and privately owned utilities will be marked out on the ground surface prior to subsurface activities. No subsurface activities will be conducted within three (3) feet of a utility mark-out, and specific utility clearances should be confirmed with the utility owner prior to subsurface activities in the vicinity.

Prior to beginning excavation or drilling, underground utilities in the vicinity of the working areas shall be identified via one of the following three lines of evidence

- Contact the State One Call
- Obtain a detailed site utility plan drawn to scale, preferably an "as-built" plan
- Conduct a detailed visual site inspection

In the event that one or more of the above lines of evidence cannot be conducted, or if the accuracy of utility location is questionable, a minimum of one additional line of evidence will be utilized as appropriate or suitable to the conditions. Examples of additional lines of evidence include but are not limited to:

- Private utility locating service
- Research of state, county, municipal, or private utility records and maps including computer drawn maps or geographical information systems (GIS)
- Contact with the utility provider to obtain their utility location records
- Hand augering or digging
- Hydro-knife
- Air-knife
- Radio Frequency Detector (RFD)
- Ground Penetrating Radar (GPR)
- Any other method that may give ample evidence of the presence or location of subgrade utilities.

4.2 Sampling Precautions

Special care must be taken at all times not to contaminate the samples. All sample containers will be packed in a cooler on ice or ice packs to maintain the holding temperature of 4 degrees C or less and stored in a secure location to preclude conditions which may alter the properties of the sample.

A clean-pair of new, non-powdered, disposable gloves shall be worn each time a different sample is collected. The gloves should be put on immediately prior to sample collection, they should not come in contact with media being sampled, and should be changed any time during sample collection when their cleanliness is compromised.

Sample containers with samples suspected of containing high concentrations, particularly for volatile organic compounds (VOCs), shall be handled and stored separately. Likewise, all background samples shall be segregated from obvious high-concentration or waste samples. Sample collection

activities shall proceed progressively from the least suspected contaminated area to the most suspected contaminated area.

If possible, one member of the sampling team should take all the notes and photographs, fill out tags, et cetera, while the other member(s) collect the field samples.

The ground surface should be cleared of vegetation, rocks, leaves, debris, or other surface obstructions that may interfere with soil sample collection prior to sampling. If ornamental vegetation must be disturbed, e.g., grass removal, a shovel should be used to remove a layer of the turf to accommodate the sampling of underlying soils. The turf should be replaced upon the completion of the sampling.

Samples containers should be filled in a descending order from most to least likely to losses via mass-transfer mechanisms, such as volatilization. The preferred order for common analytical parameters is as follows:

- Volatile Organic Compounds;
- Semi-Volatile Organic Compounds;
- Total Petroleum Hydrocarbons;
- Total Organic Carbon;
- Metals and other Inorganics; and
- Radionuclides.

4.3 Sample Collection

4.3.1 Sample Collection for VOC Analysis

Samples collected for VOC analysis are typically collected using a TerraCore® Sampling Kit or other EPA SW-846 Method 5035A compatible container. VOC samples shall always be collected directly from the sampling location and should never be collected after homogenization or compositing.

The syringe provided in each TerraCore® Sampling Kit shall be used to collect approximately 5 grams of soil directly from the sample interval. With the plunger seated in the handle, push the TerraCore® sampler into the exposed sample interval until the chamber is filled. A filled chamber will deliver approximately 5 grams of soil. The soil plug collected should be flush with the open end of the sampler. Wipe away all solids and debris from the sampler as quickly as possible. Remove any excess solids that extend beyond the opening of the chamber.

The TerraCore® Sampling Kit, provided by the laboratory, contains three 40 mL vials (two containing deionized water and one containing methanol) and an unpreserved 2 oz. soil jar. A 5

gram sample of the soil from the syringe shall be placed into each of the 40-mL vials provided by the laboratory. The fourth unpreserved soil jar can be filled without using the syringe. This unpreserved jar is used to calculate the dry weight of the soil.

Rotate the plunger that was seated in the handle 90° until it is aligned with the slots in the body. Place the open end of the sampler into the 40-mL vial(s) containing the applicable preservative and slowly extrude the soil plug by pushing the plunger down. Wipe away any soil or debris from the threads of the vial (s) and quickly place the cap back onto the vial.

All soil samples must be placed in the laboratory approved sample containers immediately to reduce volatilization losses. After collection of the sample into the vial or other container, the sample must be stored in an ice chest and cooled.

Syringe - Add about 3.7 cc (approximately 5 grams) of sample material to 40-mL pre-prepared containers. Secure the containers in a plastic bag. Do not use a custody seal on the container; place the custody seal on the plastic bag. Note: When using the syringes, it is important that no air is allowed to become trapped behind the sample prior to extrusion, as this will adversely affect the sample.

4.3.2 Sample Collection for Inorganic and Non-Volatile Organic Analysis

Samples collected for non-volatile analyses, should be homogenized in a dedicated or decontaminated stainless-steel or glass mixing bowl. Homogenization should be completed via thorough hand mixing of the sample with a pre-cleaned decontaminated trowel, spoon, or shovel.

If a composite (or multi-increment) sample of several surface locations is desired, or if homogenization of a vertical sample from a single location is necessary to generate a representative sample, then mixing must be performed using a decontaminated or dedicated glass or stainless steel bowl. Compositing and mixing will be performed only after any samples to be submitted for analysis of VOC have been taken. Multi-increment sampling, if conducted, will be completed via collection of field composite samples. When compositing, make sure that all composite locations (aliquot) consist of equal volumes. Only three-point composites will be acceptable, and may be used to achieve sampling coverage for very large parcels.

4.4 Sample Collection Methods

4.4.1 Spoons

Stainless steel spoons or plastic may be used for surface soil sampling to depths of up to approximately 12 inches below ground surface where conditions are generally soft and non-indurated, and there is no problematic vegetative layer to penetrate.

When using stainless steel spoons, consideration must be given to the procedure used to collect the volatile organic compound sample. If the soil being sampled is cohesive and holds its in situ texture in the spoon, the syringe used to collect the sub-sample for Method 5035A should be plugged directly from the spoon. If, however, the soil is not cohesive and crumbles when removed from the ground surface for sampling, consideration should be given to plugging the sample for Method 5035A directly from the sample location.

4.4.2 Hand Augers

When conducting surface soil sampling with hand augers, the auger buckets may be used with a handle alone or with a handle and extensions. The bucket is advanced to the appropriate depth and the contents are transferred to the homogenization container for processing or the sample is collected directly from the bucket.

Hand augers are the most common equipment used to collect shallow subsurface soil samples. Auger holes are advanced one bucket at a time until the sample depth is achieved. When the sample depth is reached, the bucket used to advance the hole is removed and a clean bucket is attached. The clean auger bucket is then placed in the hole and filled with soil to make up the sample and removed.

The practical depth of investigation using a hand auger depends upon the soil properties and depth of investigation. In sand, augering is usually easily performed, but the depth of collection is limited to the depth at which the sand begins to flow or collapse. Hand augers may also be of limited use in tight clays or cemented sands. In these soil types, the greater the depth attempted, the more difficult it is to recover a sample due to increased friction and torqueing of the hand auger extensions. At some point these problems become so severe that power equipment must be used.

Because of the tendency for the auger bucket to scrape material from the sides of the auger hole while being extracted, the top several inches of soil in the auger bucket should be discarded prior to placing the bucket contents in the homogenization container for processing.

4.4.3 Manual Collection via Hand Augers

Hand augers may be used to advance boreholes and collect soil samples in the surface and shallow subsurface intervals. Typically, stainless steel auger buckets with cutting heads are used. The bucket is advanced by simultaneously pushing and turning using an attached handle with extensions (if needed). VOC samples should be collected directly from the auger bucket, if possible.

When conducting surface soil sampling with hand augers, the auger buckets may be used with a handle alone or with a handle and extensions. The bucket is advanced to the appropriate depth and the contents are transferred to the homogenization container for processing.

Power augers may be used to advance boreholes to depths for subsurface soil sampling with the hand auger; however, they may not be used for sample collection. When power augers are used to advance the borehole to depth for sampling, care must be taken that exhaust fumes and/or oil do not contaminate the borehole or area in the immediate vicinity of sampling.

When moving to a new sampling location, the entire hand auger assembly must be replaced with a properly decontaminated hand auger assembly, or cleaned and decontaminated in accordance with SOP 016 - Equipment Decontamination.

Upon completion of sampling at any given location (whether a subsample for a composite, or a stand-alone grab sample), the location should be clearly marked with a stake and flagging tape or a pin flag. The sample location number shall be marked on the stake (or flag) using indelible ink. The sample location should be photographed for documentation purposes. Hand-held GPS units are typically suitable for documenting sample locations to the desired degree of accuracy and, routinely, coordinates should be obtained and recorded at the time of sampling if so specified in the project planning documents. If very accurate survey information is required, the sample location shall be surveyed at a later time unless sample locations were laid out in advance via surveying.

5 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance and quality control for surface soil sampling activities will consist of several distinct elements. Double checking of planned sample numbers versus numbers recorded on the field log sheets, on the sample label, and on the chain-of-custody form shall be completed to ensure accuracy.

All relevant observations and information about the sample location and sample collection effort shall be recorded in the field logbook in accordance with the field logbook SOP. Detailed information regarding the sample and required analysis shall be recorded on a surface soil sample form, including, but not limited to, sample number; collection date, time, and location; soil texture and color; and relevant observations for the sample location (staining, odors, stressed vegetation) An example surface soil sample form is provided for reference.

Upon collection, all samples will be managed in accordance with SOP 011 - Sample Handling, Packing, Shipping, and Chain of Custody. Once samples have been placed into the appropriate sample containers, sample ID, sample location, and sample date and time of collection should be recorded on the sample label. This information shall be consistent with what is recorded on the chain-of-custody (COC).

All sample containers will be packed in a cooler on ice or ice packs to maintain the holding temperature of 4 degrees C or less.

SOP No. 009
SUBSURFACE SOIL SAMPLING
STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

This Standard Operating Procedure (SOP) presents procedures for the collection and identification of representative subsurface soil samples from borings. Soil samples are used to evaluate the physical and/or chemical characteristics of the subsurface. Physical information can be used to define site geologic, hydrogeologic, and geotechnical properties. Chemical data generated from these samples can be used to define the lateral and vertical extent of contaminants in the subsurface.

Samples may be collected *via* a number of techniques, depending upon site conditions and project objectives. These techniques include split-barrel sampling or thin-walled sampling through hollow-stem augers, direct-push sampling *via* Geoprobe or cone-penetration technology, hand auger, test pit excavation, or other methods.

Unless otherwise specified in specific task work plans, subsurface soil at depths of 1 ft to 10 ft below ground surface (bgs) will be characterized by sampling at intervals of 4-5 ft bgs and 9-10 ft bgs, unless field conditions prevent the collection at a depth of 9-10 ft bgs. Data derived from subsurface soil sampling can be used to:

- Determine whether a release of constituent(s) of interest has occurred
- Delineate the nature and extent (both lateral and vertical) of a release
- Provide information to support an assessment of potential groundwater impacts
- Establish background concentrations of naturally occurring constituents (i.e., metals)
- Support remedial design activities

2 EQUIPMENT

Equipment may vary depending on specific project objectives. Sampling equipment may consist of:

- Split-barrel sampler
- Thin-walled sampler
- Direct-push sampler
- Core-barrel sampler

These sampling devices will generally be provided by subcontractors.

Project planning documents should be reviewed by field personnel and Field Team Leader to determine the types of sampling equipment required for completion of the designated tasks. The types of equipment to be used may vary based on the location of the site, and State- or EPA Region-specific requirements. Examples of other relevant equipment for subsurface soil sampling may include:

- Health and Safety Plan
- Work Plan
- Hard Hat
- Safety Glasses
- Steel Toed Work Boots
- Hearing Protection
- Safety Vests
- Daily Mobile Equipment Check List
- Tailgate Safety Meeting Sheets
- Direct Push Drilling Equipment
- Hand Augers
- AMS Soil Probes
- Wildco Hand Corer Sampler
- Acetate Sample Sleeves
- Soil Cone Catches
- Spoons
- Spatulas
- Bowls
- Plastic Sheeting
- Sample Bottles
- Photoionization Detector
- Buckets
- Scrub Brushes
- Detergents (Non-phosphate)
- Potable Water
- Deionized Water
- Nitric Acid
- Hexane
- Spray Bottles (for Decon)
- Clipboard
- Chain-of-Custody Forms
- Sample Collection Forms
- Field Logbook
- Sample Labels
- Air Bills
- Shipping Labels
- Custody Seals
- Indelible Ink Pens
- Zip-Lock Type Bags
- Trash Bags
- Bubble Wrap
- Vermiculite
- Cooler(s)
- Ice/Freezer Packs
- Duct Tape
- Strapping Tape
- Nitrile Gloves
- Paper Towels / Shop Cloths
- 55-Gal DOT-Approved Steel Drums
- Drum Labels
- Digital Camera
- Stakes
- Pin Flags
- Pedometer
- Flagging Tape
- Marking Paint
- Hand-Held GPS Unit
- Metal Detector or Utility Locator
- Tape Measure (100' – 300' reel)
- Compass

3 LOCATIONS

Borings and test-pits should be collected at or as close as possible to the locations and depths provided in project work plan. Locations shall be confirmed via the use of a hand-held GPS unit and staked prior to drilling or excavating. Otherwise, sample locations shall be staked by a licensed surveyor prior to mobilization.

If required, the proposed locations may be adjusted in the field, based on site access, property boundaries, and surface obstructions. Sample locations where refusal is encountered prior to reaching target depths shall be relocated as close as reasonably possible to the original sample location, unless otherwise directed by the project manager. The location of the boring shall be recorded on the boring log via the use of a hand-held GPS unit or with survey coordinates, where available. The project manager shall be notified if a representative boring cannot be located near the locations provided in the project work plan.

3.1 Cautions

Underground utility locating will be conducted prior to all subsurface exploration. All public and privately owned utilities will be marked out on the ground surface prior to subsurface activities. No subsurface activities will be conducted within three (3) feet of a utility mark-out, and specific utility clearances should be confirmed with the utility owner prior to subsurface activities in the vicinity.

Prior to beginning excavation or drilling, underground utilities in the vicinity of the working areas shall be identified via one of the following three lines of evidence:

- Contact the State One Call
- Obtain a detailed site utility plan drawn to scale, preferably an "as-built" plan
- Conduct a detailed visual site inspection

In the event that one or more of the above lines of evidence cannot be conducted, or if the accuracy of utility location is questionable, a minimum of one additional line of evidence will be utilized as appropriate or suitable to the conditions. Examples of additional lines of evidence include but are not limited to:

- Private utility locating service
- Research of state, county, municipal, or private utility records and maps including computer drawn maps or geographical information systems (GIS)
- Contact with the utility provider to obtain their utility location records
- Hand augering or digging
- Hydro-knife
- Air-knife

- Radio Frequency Detector (RFD)
- Ground Penetrating Radar (GPR)
- Any other method that may give ample evidence of the presence or location of subgrade utilities.

Overhead power lines also present risks and the following safe clearances must be maintain from them in accordance with American National Standards Institute (ANSI) Standard B30.5-1994, 5-3.4.5.

Power Line Voltage Phase to Phase (kV)	Minimum Safe Clearance (feet)
50 or below	10
51 to 200	15
201 to 350	20
351 to 500	25
501 to 750	35
751 to 1000	35

4 PROCEDURES

4.1 Drilling Procedures

The drilling contractor will be responsible for obtaining accurate and representative samples; informing the supervising geologist of changes in drilling pressure; and keeping a separate general log of soils encountered, including blow counts (i.e., the number of blows from a soil sampling drive weight [140 pounds] required to drive the split-barrel sampler in 6-inch increments). Records will also be kept of occurrences of premature refusal due to boulders or construction materials that may have been used as fill. Where a boring cannot be advanced to the desired depth, the boring will be abandoned and an additional boring will be advanced at an adjacent location to obtain the required sample. Where it is desirable to avoid leaving vertical connections between depth intervals, the borehole will be sealed using cement and/or bentonite.

Multiple refusals may lead to a decision by the supervising geologist to abandon that sampling location.

4.2 Sample Collection

Subsurface soil samples can be collected using a variety of methods that are generally dependent upon project requirements, intended analyses (*i.e.*, volume of soil required for testing) and site geologic conditions. Common sample collection methods are discussed below:

4.2.1 Split-Barrel Sampling

The procedures for this sampling method are presented in the American Society for Testing and Materials (ASTM) Method D1586. The samples collected with this method usually provide a sufficient volume to test some physical parameters, such as grain size distribution, and commonly performed chemical analyses (*e.g.*, VOCs, SVOCs, and metals).

Following each use, the sampler should be washed thoroughly to remove residual soils. If samples are to be submitted for chemical analysis, the sampler should be decontaminated in accordance with SOP 016 between samples using a soapy (nonphosphatic) water wash and clean water rinse followed by solvent rinses and/or acid rinses and distilled water rinses as required for the analytes of interest.

Split-barrel samples are used to collect soil samples 18 to 24 inches in length from a selected depth interval. Depth intervals will be specified in the project-specific work plan. The sampling spoon should have a cutting shoe in good condition, and a vented head to release air and water pressure during driving. Metal or plastic retainers should be used to retain soil samples. The sampling depth and the blow counts for each 6-inch interval will be recorded on the boring log. After removing the sampler from the borehole, these procedures should be followed:

- Note and record the amount of recovery
- Describe the sample as per ASTM Method D2488 (See SOP No. 012 – Geologic Logging)

Select representative portion(s) for retention and place in a labeled clean storage jar(s) for subsequent evaluation of physical characteristics or in a laboratory supplied, labeled jar for laboratory chemical analysis.

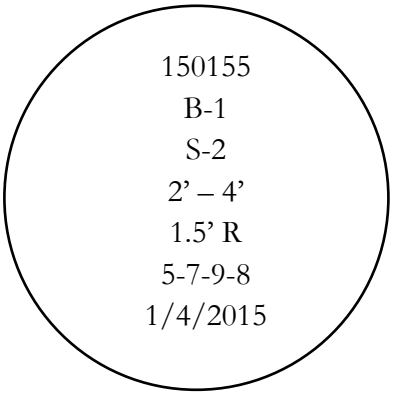
If samples are to be field screened for volatile organics: (1) the soil core should be screened immediately after the spoon is opened; and/or, (2) a sample should be placed with adequate headspace in a clean glass jar to be screened later for volatile organic chemicals in the headspace, if necessary. If a sample is to be submitted for volatile organic chemical analysis, it is important that exposure time of the soils to the air be kept to a minimum. In addition, samples collected for chemical analysis should be placed on ice in a sample cooler immediately after sampling. Samples collected for VOC analysis should be collected as prescribed in *SOP No. 008 Surface Soil Sampling.*

As necessary, the following information should be included in the boring log:

- Sample depth interval
- Blow counts required for each six-inch penetration
- Sample recovery
- Sample description
- Field screening data

When samples are collected for laboratory analysis, include the unique sample identification number, the type of analyses requested, and the laboratory where the sample is to be sent.

Samples collected for physical testing should be collected from a representative section of the spoon sample. This sample must be placed in a jar of sufficient size to hold a 5-inch long, 2-inch diameter sample, and have a cap with a gasket to seal in moisture. The jar cap must be labeled with the Project No., Boring No., Sample no., Depth of sample, Recovery, Blows per 0.5-foot penetration, and the date the sample was collected. The example below displays the appropriate format.



Sample Jar Lid

4.2.2 Undisturbed (Thin-Walled) Soil Sampling

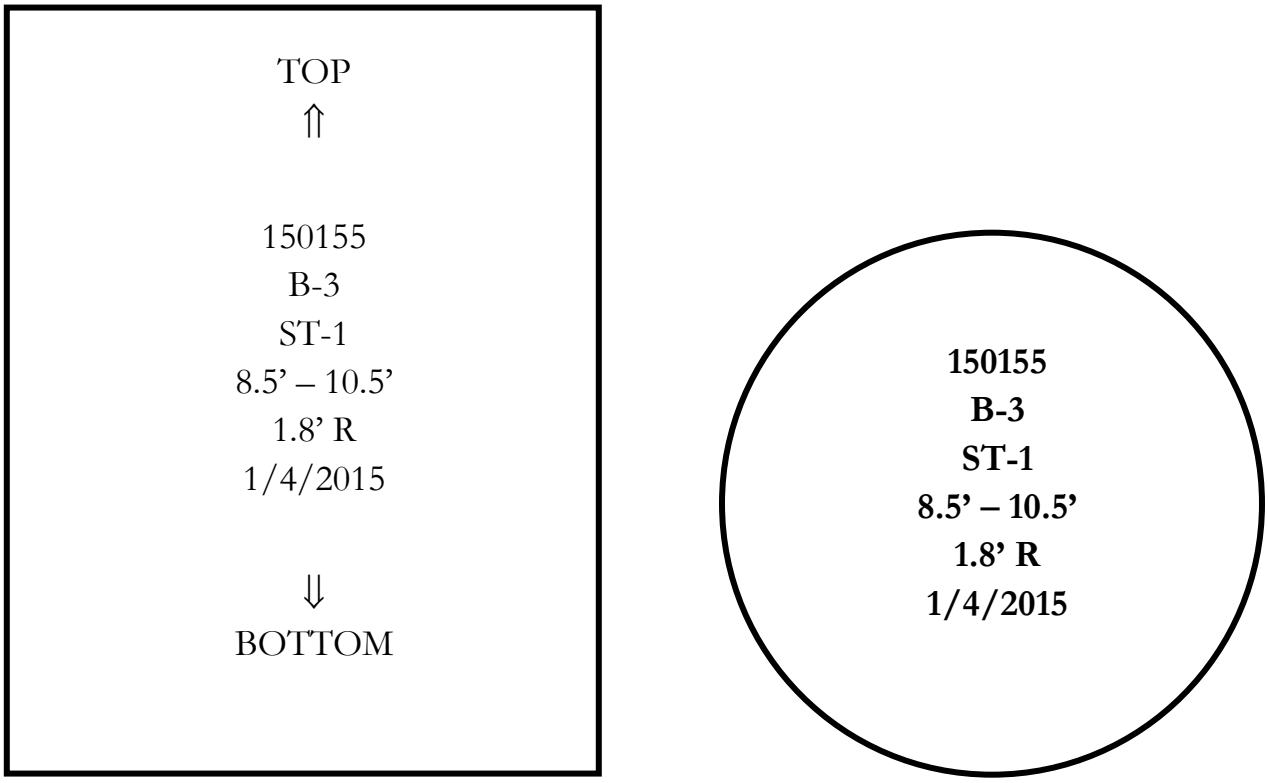
These samples are commonly referred to as "Shelby tube" samples. The method is used to collect samples in conjunction with auger or wet rotary drilling methods, generally for geotechnical testing, but they may be used for chemical analysis as well. These samples are generally collected only from cohesive materials.

Typically, the soil is not removed from the Shelby tube in the field, unless analytical testing is required; the tube ends are sealed with plastic caps and/or wax and the tube sent intact to the testing laboratory. Prior to sending the samples to the laboratory, all residual soil should be removed from the outside of the sampling tube.

The tube should then be prepared for shipment as indicated in ASTM Method D1587, and labeled as shown below, with the following information:

- Job name and number
- Sample location (soil or well boring number)
- Sample identification
- Sample interval and the percent recovery
- Date of sample
- Top and bottom of sample - lines should be drawn around the circumference of the tube, indicating the top and the bottom of the sample with an arrow pointing toward the top

This information and any descriptive data on sample characteristics should be recorded in the field notebook.



Shelby Tube Labeling (Tube and Cap)

4.2.3 Direct-Push Soil Sampling

The Geoprobe® direct-push soil sampling methodology is described herein, and is considered to be representative of most direct-push soil sampling procedures. Direct-push soil borings are completed by hydraulically pushing a sampling device to the top of the desired depth interval for soil sample collection. The soil sampling device typically consists of a stainless steel sampling tube through which a stainless steel drive point is inserted and attached to a piston stop pin. The steel drive point and piston stop pin prevent soil from entering the sampling device until the desired depth interval is encountered. A dedicated acetate liner for soil containment may be inserted into the sampling device. When the top of the desired sampling interval is encountered, the piston stop pin and stainless steel drive point are removed in order to permit soil to enter the sampling device with the next push of the rods. The rods are then extracted and the sampling device is opened to expose the sampled core of soil, which can then be described and/or containerized.

4.2.4 Roto-Sonic Drilling

Sonic drilling employs the use of high frequency resonant energy to advance a core barrel or casing into subsurface formations. With dual wall casing, continuous cores are collected and removed as drilling progresses. Sonic drill rigs can penetrate cobbles, boulders, and rock. Large-diameter continuous cores of almost any soil type can be collected without the use of drilling fluids, such as air or water-based fluids and additives. Drilling and sampling are possible through wood, concrete, and other construction debris. The sonic-drilling system can drill and sample softer rock, such as sandstone, limestone, shale, and slate with a high rate of core recovery. Drilling can be faster than most other drilling methods, depending on depth and material drilled. Uniform boreholes with minimal drift are ideal for monitoring-well installation and corresponding well development time. Investigation-derived waste is also minimized with sonic drilling. Plastic or acetate liners should be used inside the core barrels for sample collection.

After soil core recovery, examine the soil core for lithology. Depending on project-specific objectives, the soil core may be screened for VOCs using a PID or FID. The core will then be logged and sampled for geotechnical or analytical testing.

5 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance and quality control for subsurface soil sampling activities will consist of several distinct elements. Double-checking of planned sample numbers versus numbers recorded on the field log sheets, on the sample labels and on the chain-of-custody forms shall be completed to ensure that no mix-up of samples versus locations occurs. Collection of field quality control samples will be completed as specified in QAPP Worksheet 20.

Decontamination of sampling equipment between sample locations is to be performed as outlined in SOP 016.

All relevant observations and information about the sample location and sample collection effort shall be recorded in the field logbook in accordance with the field logbook SOP. Detailed information regarding the sample and require analyses shall he recorded on a soil sample collection form, including, but not limited to, sample number, collection date/time, sample location, soil texture/color, relevant observations such as staining, odors, and PID readings. A soil sample form is provided at the end of this SOP. All boring logs shall be compiled as presented in the geologic logging SOP.

SOP No. 010
FIELD LOGBOOK
STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

This Standard Operating Procedure (SOP) describes the procedures and requirements for entering information in a field logbook maintained for environmental investigations. The field logbook will act as the primary source of documentation for field activities. Moreover, the field logbook(s) may serve as the primary legal record of field operations and any occurrences associated with those operations. The requirements and procedures set forth in this SOP are designed to ensure that all field activities are sufficiently and properly documented.

This SOP is not designed to specifically address all of the entries that may be required for a given project. It is intended to supplement project-specific documentation; including work plans, sampling and analysis plans, health and safety (H&S) plans, quality assurance project plans, and additional SOPs, as appropriate, in order to ensure proper documentation.

It is the responsibility of the project manager and the field team leader to ensure that field logbook entries provide sufficient information for the completion of a detailed and accurate description of all field operations. Complete, detailed, and accurate field log book entries are essential to:

- Ensure that the level of data collection associated with field activities is sufficient to support the successful completion of the project;
- Ensure that all changes or deviations from project work plans are documented;
- Ensure that quality control is maintain over the duration of the project;
- Ensure that the administrative requirements of the project are met;
- Ensure that there is sufficient information so that a detailed summary of field activities can be independently compiled by non-project affiliated personnel at a later date; and
- Ensure that an accurate record of field operations can be presented in any legal proceedings that may arise.

The field team leader managing field logbook(s) should have a minimum of one (1) year of field experience. In addition, all field personnel shall be versed in the SOPs relevant to their specific tasks and possess the required skills and experience necessary for the successful completion of the desired field operations.

2 EQUIPMENT

The required materials for documentation of field activities in the field are presented below.

- Permanently bound, water-resistant notebook.
- Indelible ink ball point pen or fine-tipped Sharpie® pen.
    - Ink shall not bleed through the page and become visible on the reverse side of the page,
    - In the instance where weather conditions preclude the use of a pen, indicate so in the field logbook and use an alternate writing instrument.
- Ziploc® baggie or other weather-proof container to protect the field logbook from the elements.

3 PROCEDURES

Field personnel should be familiar and compliant with the site-specific or project-specific Health and Safety Plan (HASP) prior to undertaking field operations. All requirements of the HASP should be maintained for the duration of the field work.

All entries in the field log must be legible and archivable. The field logbook should never be exposed to the elements or conditions that may moisten the pages and smear the ink. When not in the field, the field log book shall be stored in a location where it will be easily accessible to field crews. Each field crew shall maintain a single log book. The field manager is responsible for ensuring that the field crews properly follow the procedures provided herein.

All entries shall be made in English and legible non-cursive print. On the front cover of the field logbook the following shall be recorded in indelible ink:

- Project Name;
- Project Number;
- Project Location;
- Project Phase (if applicable);
- Title and Date of Work Plan being followed:
- Applicable Appendix A Field SOP referenced in the Work Plan (field personnel must have copies of these SOPs in the field);
- The date field activities associated with that logbook commenced;
- The date field activities associated with that logbook; and

- If more than one logbook is associated with the project or project phase, the record number of the logbook, e.g., Book 1 of 2, or Vol. 1 of 2.

On the inside front cover of the logbook, include the following in indelible ink:

- "If found, please return to [Company Name]";
- The appropriate return address and associated phone number;
- The name of the person to which the field logbook is assigned; and
- The name of the project manager.

The first page of the logbook shall be reserved for a table of contents. If the first page of the logbook is a title page, reserve the second page for a table of contents. The last five (5) pages of the logbook shall be reserved for important contacts, notes, reminders, health and safety information, et cetera. If the pages are not pre-numbered, the field manager or designee shall number the front and back of each page at the bottom of the page.

For each day of field work, the following should be recorded in the field logbook, as applicable:

- The month, day, and year at the top right hand corner of the next available full page;
- The project name;
- Time of arrival;
- Name and affiliation of the person keeping the logbook;
- Work site location;
- Names and affiliations of any people on-site related to the project, including contractors, subcontractors, visitors, agency personnel, client representatives, etc. and their time of arrival and time of departure;
- A brief description of the work to be performed;
- A list of active equipment on-site;
- Prevailing weather conditions and weather-related delays;
- A brief summary of any H&S meetings or tailgate meetings;
- Any special precautions taken with regard to H&S;
- A record of instrument calibrations and checks;
- A record of any approvals for field changes to the scope of work;
- A record for the basis of field changes to the scope of work;

- Sampling event descriptions, including methodologies, sample numbers and volumes, descriptions of samples, time of collection, and name of collector;
- Technical measurements made in the field including indications of anomalous measurements;
- A record of any project related phone calls;
- A record of any project related meetings on-site;
- References to GPS or survey data used or collected;
- Descriptions of equipment used in field activities;
- Maps, diagrams, or sketches as needed to document sample locations;
- A record of any downtime, the basis for such downtime, and any corrective measures employed;
- Equipment issues encountered and the resolution of such issues;
- Any pertinent factual observations, including the collection of QA/QC samples, damage to equipment or sampling locations; accidents, field personnel overtly not following direction, et cetera.
- Management and disposal of any investigation derived wastes.
- A record of significant photographs taken, including camera used, photographers name, and direction and view angle of the photographs;
- Periodic time entries on the left hand side of the page to reference entries in the field book without a timestamp; and
- Time of departure

At the end of each day, the person keeping the logbook or designee shall sign and date each page where entries were made for that day. Unused space at the end of page shall be marked with a diagonal line, signed, and dated. Entries for the subsequent day shall begin on the next full available page. The field team leader shall also sign and date the final daily entry page of each field crew's logbook, after verify the day's activities.

Field logbook entries shall be made in the field at the site, as close as possible to the correlated observation, not at a later time or different location. Supplemental entries to the logbook may be made at a later time. All supplemental entries must be clearly identified as such, with the basis for the supplemental entry clearly stated. Supplemental entries shall be signed and dated by the person making the entry and the field team leader.

If any entry to the logbook is changed, strike out the deleted text or item with a single line such that the entry remains legible, initial, and date the change. Changes should only be made by the person that made the initial entry.

Problems identified in the field logbook must be brought to the attention of the project manager or the field team leader as soon as possible. Problems may be reported in person or on the telephone and a record of the conversation shall be maintained in the logbook. In the instance that the problem does not need immediate resolution, i.e., it does not affect health, safety, the environment, or the effective continuation of work; the problem may be recorded on a daily log form and transmitted to the project manager or field team leader that day.

4 QUALITY ASSURANCE

Each completed page of the field logbook must be scanned for electronic archiving at periodic intervals, and at a minimum on weekly basis. This will ensure that copies of the field notes are available in the event the field logbook is lost or damaged, and that in such an event the loss of data is minimal. It will also ensure that field data can easily be disseminated without the risk of physically sending the field logbook. The project manager shall review the scanned copies of the field notes as they become available to ensure legibility and that data quality objectives are met. Field logbook scans will be included in applicable data reports to EPA Region III and MDE.

Completed field logbooks should be archived with the project files, if completed field logbook entries are needed in the field for continued operations, this data should be available as copies and not the original completed field logbook.

As always, project personnel should be mindful that the field logbook may be produced in court.

SOP No. 011
SAMPLE HANDLING, PACKING, SHIPPING AND CHAIN-OF-CUSTODY STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) describes the procedures and requirements for sample management; including chain-of-custody (COC), handling, packing, and shipping procedures. The purpose of this SOP is to specify sample management techniques so that the potential for cross-contamination, tampering, misidentification, sample loss, and breakage are minimized. Moreover, these techniques are designed to ensure that samples are maintained in a controlled environment from the time of collection until receipt by the analytical laboratory. This SOP is generally applicable for the collection of aqueous and solid samples (e.g., soil, sediment, or sludge). Detailed handling procedures for soil gas and air samples are provided in the relevant SOPs; however the shipment and chain-of-custody procedures for those samples shall be governed by the requirements herein.

2 EQUIPMENT

The following list provides materials that may be required for each project where samples are to be collected. Project-specific documents and sample collection requirements should be reviewed prior to initialize field operations:

- Indelible ink pens or markers (fine-tipped) of blue or black ink;
- Polyethylene re-sealable bags;
- Clear packing tape and duct tape;
- Chain-of-custody forms;
- Shipping labels, as applicable;
- Custody seals or tape;
- Gloves (disposable latex or nitrile);
- Appropriate sample containers and labels;
- Sample preservatives, if not provided in sampling containers;

- Insulated coolers;
- Wet ice of a sufficient amount to maintain 4°C temperatures during the collection and transfer of samples;
- Cushioning and shock-absorbent material, e.g., bubble wrap or air-filled packaging bags; and
- Field log book.

3 PROCEDURES

Field personnel should be familiar and compliant with the site-specific or project-specific Health and Safety Plan (HASP) prior to undertaking sample collection activities. All requirements of the HASP should be maintained for the duration of the sampling.

Field personnel should review project requirements and select appropriate supplies prior to field mobilization. This review includes ensuring that appropriate sample containers with applicable preservatives, coolers, and packing material have been supplied by the laboratory. Sample holding times should be familiarized prior to mobilization. Any analysis with holding times less than 48 hours should be specifically noted so that proper planning is initiated to ensure that these holding times are not exceeded.

Field personnel should be familiar with or should be notified by the project manager of any applicable dangerous goods shipping regulations relative to the samples being collected. This may include U.S. Department of Transportation (DOT) and International Air Transport Association (IATA) regulations. Potential samples requiring compliance with DOT regulations include Methanol-preserved volatile organic compound (VOC) soil samples and non-aqueous phase liquids (NAPL).

Some sample containers provided by the analytical laboratory contain preservatives. The preservatives must be retained in the sample container and should, in no instance, be rinsed out. Preservatives may be corrosive and standard care should be exercised to reduce the potential contact to personnel skin or clothing. If spillage is observed, project safety procedures should be followed. If the sample container caps are broken or missing, do not use the container for collection and discard the bottle.

Appropriate caution should be used when handling glass sample containers. 40 mL vials can be prone to breakage when tightening lids, particularly amber glass vials which are thinner.

3.1 Chain-of-Custody Procedures

- Prior to sample collection, complete the header on the chain-of-custody (COC) by filling in the project number, project name, contact person, sampler name, and other relevant project specific information. An example chain-of-custody is provided at the end of this SOP.

- COC entries must be printed legibly using indelible black or blue ink.
- After sample collection, enter the individual sample information on the COC.
    - Sample Identification indicates the sampling location. A sample identification (ID) system (or Station Designation Scheme) will be used to identify each environmental sample collected as described in the Data Management Plan (Appendix C of the QAPP). This ID system will provide a tracking procedure so that information about a particular sample collected from a specific location can be retrieved easily and accurately. This system also will ensure that each sample is unique and will not be confused with any other sample. The first part of the sample ID will represent the area of the Site (facility/site association) where the sample was collected. It will be comprised of two components: two letters, or a letter and a number. For example, sample locations within Parcel A1 will be given a label beginning "A1", while sample locations within the Coke Oven area will be given a label beginning with "CO". See **Table 5-1** in Appendix C of the QAPP for all location designations. The next three numerals designate the sample location number (sequential station number). The next two letters will represent the matrix and method of collection (station type/purpose). These will be designated as SB for Soil Boring, PZ for Piezometer, or MW for Monitoring Well. The final set of numbers will indicate the depth at which the sample was collected. Each part of the sample ID for a location will be separated by a dash. For example, a sample ID of A1-001-SB-05 would designate the soil sample was collected from a soil boring at Location 001 in Parcel A1 at a depth of five feet bgs, and A1-001-PZ-15 would designate the groundwater sample was collected from a piezometer at Location Number 1 in Parcel A1at a depth of 15 feet bgs.
    - List the date of sample collection. The date format to be followed should be mm/dd/yy (e.g., 01/10/15) or mm/dd/yyyy (e.g., 01/10/2015).
    - List the time that the sample was collected. The time value should be presented using 24-hr format, i.e., 3:20 p.m. should be entered as 15:20.
    - Mark in the appropriate column(s) on the COC if the sample is a composite sample (i.e., collected over a period of time or from several different locations and mixed prior to placing in the sample containers) or a grab sample (i.e., a single sample from a single time or location). The COC has a field prompting the sampler to indicate the sample was collected as a composite, by entering a "c", or a grab by entering a "g". Lower-case print should be used to avoid confusion.
    - Any preservative contained in the sampling container should be noted.
    - The analytical parameters that the samples are being analyzed will be pre-printed on the columns. If additional analyses are required, they should be written legibly on the extra columns. As much detail as possible should be presented to allow the analytical laboratory to properly analyze the samples. For example, semi-volatile organic compound (SVOCs) analyses should be represented by entering "SVOCs"

and "Method 8270D." Multiple methods and/or analytical parameters may be combined for each column (e.g., PCBs/8082,SVOCs/8270D). These columns should also be used to present sample-specific parameter lists (e.g., Appendix IX + Chromium VI). Each sample that requires a particular parameter analysis will be identified by placing the number of containers in the appropriate analytical parameter column. For metals, in particular, it may be necessary to indicate what metals are required.

- Indicate the number of containers for each method requested.
- If applicable, note which samples should be used for site-specific matrix spikes.
- Indicate any special project requirements.
- Indicate the requested turn-around time.
- Provide the relevant contact information (name, phone number, and e-mail) in the event problems or questions are encountered by the analytical laboratory.
- If applicable, provide the laboratory task order forms.
- The "Remarks" or "Comments" field should be used to present special analytical requirements to the laboratory. These may apply on an individual sample basis or for the entire sample deliverable group (SDG). Examples of remarks would be "extract and hold sample until notified" or "rush 3-day turn-around, this sample only."
- The "Relinquished by" field should be the signature of the sampler who relinquished custody to the shipping courier or analytical laboratory.
- The "Date" field following the signature block should be filled in with the date the samples were relinquished in mm/dd/yy format.
- The "Time" field should be filled in with the time, in 24-hr format, that the samples were relinquished.
- The "Received by" field shall be signed by the sample courier or laboratory representatives who received the samples from the sampler.
- Complete as many COCs necessary to properly document the collection and transfer of the samples to the analytical laboratory.
- Record the serial numbers of the COCs and time and date of sample relinquishment in the field log book.
- Upon completing the COCs, forward two copies to the analytical laboratory and retain one copy for field records.
- If electronic COCs are utilized, sign the form and make one copy for internal records. Forward the original with the samples to the laboratory.

3.2 Sample Handling

3.2.1 Sample Collection

- Clean, new, analytical sample containers and appropriate preservatives will be provided by the contracted analytical laboratory.
- Common preservatives include hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), Methanol (CH_3OH or MeOH), and sodium bisulfate ($NaHSO_4$). Samples will be preserved in accordance with method- or project- specific protocols outline.
- Disposable latex or nitrile gloves should be used to avoid cross-contamination of samples and protect against exposure to either contaminated media or preservatives.
- After the filling the respective sampling containers, with the associated sampling material and any necessary preservative, in accordance with the relevant SOP and project- or method-specific requirements, samples will be properly identified using sample container labels. The following information shall be recorded on the sample label in indelible ink:
    - Sample type or matrix, e.g., surface water (SW), soil (SO), etc.
    - Sample identification code or name;
    - Analysis required;
    - Date;
    - Time sampled;
    - Initials of the sampling personnel; and
    - Preservative added, if applicable.
- Cover the sample label with clear packing tape to secure the label onto the container and to protect the label from liquid.
- Confirm that all caps on the sample containers are secure and tightly closed.
    - It may be necessary to wrap the sample container cap with clear packing tape to prevent it from becoming loose.
- If individual custody seals are required, they should be placed on the sample container so that the cap cannot be opened without rupturing the custody seal. The custody seal should be initialed and dated prior to relinquishing the samples.
- Differing labeling procedures may be required for air samples, the relevant SOPs should be consulted for specific labeling procedures.
- After completing the sample collection procedures and sample labeling, record the following information in the field log book:
    - Project name, number and site name;
    - Sample name or identification code and sample location, if appropriate;

- Sampling method;
- Date;
- Name of the sampler(s);
- Time of collection;
- Locations of field duplicates and both sample identifications;
- Locations the field QC samples were collected including field and rinsate blanks, and additional sample volumes for matrix spikes and matrix spike duplicates; and
- Any pertinent observations or comments.

3.2.2 Packing Procedures

Following collection, all soil and aqueous samples must be placed on wet ice to initiate cooling to approximately 4°C without freezing the sample(s). Samples should be retained on ice until ready to pack for shipment to the laboratory. When preparing the samples for shipment, the following procedures shall be employed:

- If a drain plug exists on the cooler, it should secured on both the inside and outside with duct tape.
- Plastic bubble wrap or other shock absorbent material shall be placed over the bottom and corners of the cooler or shipping container.
- Wrap glass sample bottles in bubble wrap.
- Place each sample bottle upright inside the cooler. VOC vials for each sample should be rubber-banded together.
- Place cold packs or ice into the cooler. If the cooler is to be shipped via a delivery service, ensure that cold packs and ice are placed in resealable heavy-duty Ziploc® or similar.
- Samples placed on ice will be cooled and maintained at a temperature of approximately 4°C without freezing the sample(s).
- Fill the remaining space in the cooler with shock absorbent material such as bubble wrap. The cooler must be securely packed and cushioned in an upright position.
- In order to comply with 49 CFR 173.4.a.(8), the filled cooler must not exceed 64 lbs.
- Place the completed chain-of-custody(ies) in a large resealable bag and place in the cooler.
- If an independent courier service is transporting the cooler or shipping container, mark on the shipping container "Fragile" and "this side up" as appropriate. Place custody seal tape over the front and at least one side of the cooler lid, initial and date then cover with clear packing tape. Close the cooler lid and fasten the lid with packing or duct tape. Wrap packing, duct or strapping tape around both ends of the cooler.

- If project personnel or laboratory couriers are transporting the shipment directly to the analytical laboratory by automobile, periodic changes of ice may be required. In this case custody seals should not be used and limited tape should be utilized to fasten the lid. However, if the cooler is to be left unattended for any period of time, custody tape should be used.

3.2.3 Shipping Procedures

- All samples will be delivered by an express (overnight) carrier within 48 hours of sample collection or as required by analytical holding times. Alternatively, samples may be delivered directly to the analytical laboratory or a laboratory courier may be used for sample pick up.
- If parameters with short holding times are required (e.g., VOCs taken with an EnCore™ Sampler, nitrate, nitrate, and BOD), sampling personnel will take the necessary steps to ship or deliver samples to the laboratory so that the holding times will not exceeded.
- Samples must be maintained at 4° ± 2°C without freezing until receipt at the laboratory.
- All shipments must be in accordance with DOT regulations
- Upon receipt, laboratory personnel will complete the chain-of-custody by recording the data and time of receipt of the samples, measuring and noting the internal temperature of the shipping container, and ensuring sample identifications on the container labels correspond to the sample identifications and quantities provided on the chain-of-custody.
- Deviations between the chain-of-custody and the sample containers, broken containers, or temperature exceedances will be reported to the project manager immediately by the laboratory.

4 QUALITY ASSURANCE

Following each day of sample shipment, chain-of-custody records shall be transmitted to the project manager, unless otherwise directed. The sampling team leader shall retain copies of the chain-of-custody(ies) for filing in the project file. Shipping receipts and notifications, whether physical or electronic shall be maintained with the project file. A description of sample packaging and shipping information shall be made in the field log book. Laboratory reports will contain chain-of-custody records.

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Pace Analytical™ www.pacelabs.com

Page: of

Section A — **Required** Client Information:

Company:	EnviroAnalytics Group
Address:	1430 Sparrows Point Blvd
	Sparrows Point, MD 21219
Email To:	jcalenda@enviroanalyticsgroup.com
Phone: 314-620-3056	Fax:
Requested Due Date/TAT:	

Section B — **Required** Project Information:

Report To:	James Calenda
Copy To:	
PO Number:	
Project Name:	
Project Number:	

Section C — Invoice Information:

Attention:	Laura Sargent
Company Name:	EnviroAnalytics Group
Address:	1650 Des Peres Road, Suite 303 St. Louis, MO 63131
Pace Quote Reference:	
Pace Project Manager:	Samantha Bayura
Pace Profile #:	

REGULATORY AGENCY

☐ NPDES ☐ GROUND WATER ☐ DRINKING WATER

☐ UST ☐ RCRA ☐ OTHER _____

Site Location — ***STATE:*** MD

Section D — **Required** Client Information

SAMPLE ID
(A-Z, 0-9 / ,-)
Sample IDs MUST BE UNIQUE

Valid Matrix Codes

MATRIX	CODE
DRINKING WATER	DW
WATER	WT
WASTE WATER	WW
PRODUCT	P
SOIL/SOLID	SL
OIL	OL
WIPE	WP
AIR	AR
OTHER	OT
TISSUE	TS

Requested Analysis Filtered (Y/N)

ITEM #	MATRIX CODE (see valid codes to left)	SAMPLE TYPE (G=GRAB C=COMP)	COLLECTED: COMPOSITE START DATE	COLLECTED: COMPOSITE START TIME	COLLECTED: COMPOSITE END/GRAB DATE	COLLECTED: COMPOSITE END/GRAB TIME	SAMPLE TEMP AT COLLECTION	# OF CONTAINERS	Preservatives: Unpreserved	Preservatives: H_2SO_4	Preservatives: HNO_3	Preservatives: HCl	Preservatives: NaOH	Preservatives: $Na_2S_2O_3$	Preservatives: Methanol	Preservatives: Other	Analysis Test (Y/N)	VOC/8260B	SVOC 8270D	DRO/8015B	GRO/8015B	PCB/8082	METALS/6010C	Mercury/7471A or 7470A	Hexavalent Chromium/7196A	Total Cyanide/9012A	Oil and Grease/1664A	PCB/680		Residual Chlorine (Y/N)	Pace Project No./ Lab I.D.
1																														
2																														
3																														
4																														
5																														
6																														
7																														
8																														
9																														
10																														
11																														
12																														

ADDITIONAL COMMENTS	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME	SAMPLE CONDITIONS
Data Package Required? (Y/N):							
Data Validation Required? (Y/N):							
If data package is required, attach data package checklist.							

SAMPLER NAME AND SIGNATURE

PRINT Name of SAMPLER:

SIGNATURE of SAMPLER: | **DATE Signed (MM/DD/YY):**

Temp in °C	Received on Ice (Y/N)	Custody Sealed Cooler (Y/N)	Samples Intact (Y/N)

*Important Note: By signing this form you are accepting Pace's NET 30 day payment terms and agreeing to late charges of 1.5% per month for any invoices not paid within 30 days.

F-ALL-Q-020rev.06, 2-Feb-2007

SOP No. 012
GEOLOGIC LOGGING
STANDARD OPERATING PROCEDURE
Rev. 01

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1 SCOPE

This Standard Operating Procedure (SOP) describes the proper procedures for logging geologic descriptions of soil and rock samples during the drilling of boreholes and installation of monitoring wells or piezometers on a standardized form. The objective of logging a borehole is document the details of the soil and rock recovered from the borehole. These data are used to reconstruct the borehole's stratigraphy, which can then be correlated with similar data from other borehole. The sample collection discussed in this SOP is generally not applicable for analytical samples.

2 EQUIPMENT

Equipment may vary depending on specific project objectives. The following is a list of equipment that should, at a minimum, be present on site:

- Minimum 100' tape
- 25' tape measure
- Blank field logs/log book
- Clipboard
- Pencils and Sharpie
- Fat magic marker
- 10% HCl acid
- Pocketknife
- Pocket penetrometer (if cohesive soils are expected)
- Hard hat
- Steel-toed boots
- Hearing protection
- Safety glasses
- Orange safety vest (as appropriate)
- Work gloves
- White marking paint and/or flags and stakes
- Film and camera, digital camera, or disposable camera
- Soil Boring and Rock Coring Tracking Sheet and Daily Field Report

3 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to all subsurface exploration. All requirements of the HASP should be maintained for the duration of the field activities.

When drilling boreholes, field personnel should maintain a log that describes each borehole. An example of borehole log sheet is provided at the end of this SOP for reference. The following basic information should be entered on the heading of each log:

- Borehole/well number;
- Project name;
- Site location;
- Dates and times that the drilling was started and completed;
- Drilling subcontractor company and driller name;
- Field geologist's name;
- Drill rig type used to drill the borehole;
- Drilling Method(s) used to drill the borehole;
- Weather;
- Bit and auger size(s);
- Depth of auger/split-spoon refusal;
- Total depth of borehole;
- Water level at the time of completion, measured from the top of the inside casing,
    - 24-hr readings may be required, dependent upon project data objectives;
- Initials or name of engineer/geologist that checks the log after it is prepared; and
- A basic well location sketch, if necessary.

During the drilling of a borehole, specific technical information about the subsurface material and should be recorded on the boring log. Depending on the drilling methods, whether the material is consolidated or unconsolidated and project-specific objectives, the following technical information may be required:

- Depth that a sample was collected or encountered;
- Sample number assigned (if applicable);
- The number of blow counts required to drive the split barrel sampler 18" or 24", at 6" intervals;
- Description of soil components;
- Percent recovery of core, split-spoon, or shelby tube sample;
- Intervals where samples were taken;
- Descriptions of any anthropomorphic material observed;

- Rock Description; and
- Approximate depth of encountering the water table.

3.1 Sample Collection

Various methods can be employed for the collection of soil or rock samples for the purpose of geotechnical or analytical testing. In general, samples should be taken directly from the continuous core sampler or split spoon sampler. There are five basic types of samples to be familiar with:

- Split-spoon soil samples;
- Undisturbed Shelby-tube soil samples;
- Soil cores from direct-push or sonic drilling methods;
- Bulk soil samples; and
- Rock cores.

A record of all samples collected should also be maintained in the field logbook.

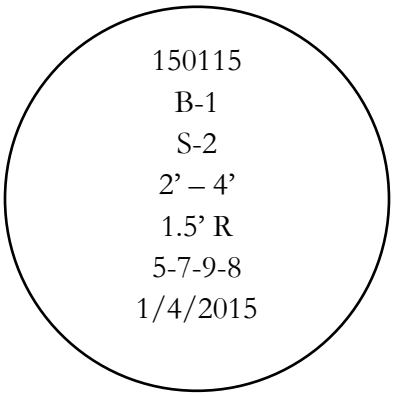
3.1.1 Split Spoon Samples

The interval at which samples are to be collected will be specified in the project documents. Follow this interval unless the Project Engineer agrees to a different one.

A 2-inch split-spoon sampler (1.5- or 2.0-foot long sampler) is driven by a 140-pound hammer free-falling through 30-inches. The field representative should be familiar with the American Society of Testing and Materials (ASTM) standard D 1586, which defines this sampling technique. The sampling spoon should have a cutting shoe in good condition, and a vented head to release air and water pressure during driving. Metal or plastic retainers should be used to retain soil samples. The ARM field representative should stay clear of this operation, so as to not interfere with the driller's work. Count the number of blows to drive the sampling spoon each 6-inch increment. This is commonly referred to as Standard Penetration Testing (SPT).

After the sampling spoon is retrieved from the borehole and opened, the ARM field representative should measure the sample recovery and note it on the Field Boring Log, a copy of which is included with this procedure. The field representative should then classify the soil. Refer to the *Sample Description* section of this document for the appropriate classification system.

A soil sample should be collected from a representative section of the spoon sample. This sample must be placed in a jar of sufficient size to hold a 5-inch long, 2-inch diameter sample, and have a cap with a gasket to seal in moisture. The jar cap must be labeled with the Project No., Boring No., Sample no., Depth of sample, Recovery, Blows per 0.5-foot penetration, and the date the sample was collected. The example below displays the appropriate format.



Sample Jar Lid

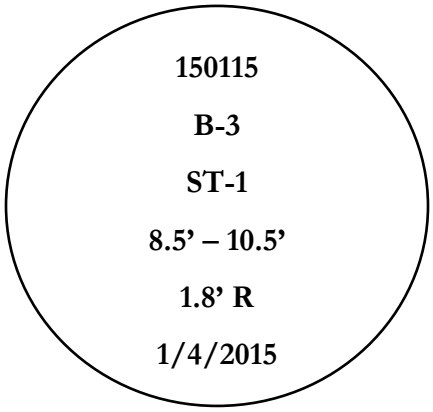
3.1.2 Shelby Tube Samples

The Shelby tube is a common technique for collecting an undisturbed soil sample from a soft, cohesive layer. The appropriate ASTM standard is D 1587. One Shelby tube should be taken per site if distinct layer(s) of cohesive (clay) soil with SPT N-values consistently less than 8 blows-per-foot. The field representative should consult the Project Engineer for specific direction.

The sample tube shall be pushed hydraulically, not driven with a hammer. Record the hydraulic pressure to push the sampler if it is available.

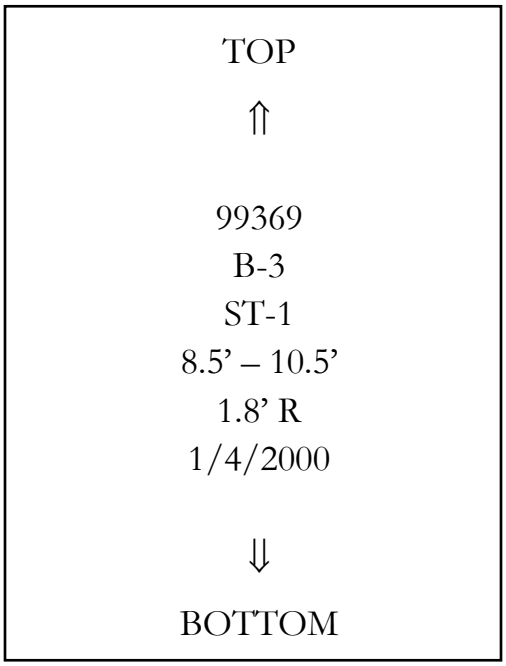
Let the sample tube rest for approximately 10-minutes in place after termination at the bottom sample depth. The actual rest period should be estimated based on the consistency and approximate shear strength of the soils.

After the tube is retrieved from the borehole, the ends should be cleaned out sufficiently to allow packing of the ends with paraffin wax. Fill any excess air space with tightly wadded paper. Cap the ends with rubber caps and tape the caps in place. Label the top end of the tube as shown below.



Shelby Tube Cap

Label the side of the tube as shown below.



Shelby Tube Label

Keep the sample vertical, orientated as it came out of the ground as much as practical during sample preparation, and always during storage and transportation. Do not allow the sample to freeze.

3.1.3 Direct Push Core Samples

Direct-push soil borings are completed by hydraulically pushing a sampling device to the top of the desired depth interval for soil sample collection. A number of sampling tools exist for direct-push borings, nearly all of which involve the collection and retrieval of the soil sample within a thin walled liner. Manufacturer and subcontractor SOPs should be followed when collecting soil cores using a direct-push rig. Three of the more common sampling methods are discussed below:

Large Bore® Sampler

The Large Bore® (LB) sampler is a solid barrel direct push sampler equipped with a piston-rod point assembly used primarily for collection of depth-discrete subsurface soil samples. The sample barrel is approximately 30-inches (762 mm) long and has a 1.5-inch (38 mm) outside diameter. The LB® sampler is capable of recovering a discrete sample core 22 inches x 1.0 inch (559 mm x 25 mm) contained inside a removable liner. The resultant sample volume is a maximum of 283 mL.

After the LB® sample barrel is equipped with the cutting shoe and liner, the piston-rod point assembly is inserted, along with the drive head and piston stop assembly. The assembled sampler is driven to the desired sampling depth, at which time the piston stop pin is removed, freeing the push

point. The LB® sampler is then pushed into the soil a distance equal to the length of the LB® sample barrel. The probe rod string, with the LB® sampler attached, is then removed from the subsurface. After retrieval, the LB® sampler is then removed from the probe rod string. The drive head is then removed to allow removal of the liner and soil sample.

Macro-Core® Sampler

The Macro-Core® (MC) sampler is a solid barrel direct push sampler equipped with a piston-rod point assembly used primarily for collection of either continuous or depth-discrete subsurface soil samples. Although other lengths are available, the standard MC® sampler has an assembled length of approximately 52 inches (1321 mm) with an outside diameter of 2.2 inches (56 mm). The MC® sampler is capable of recovering a discrete sample core 45 inches x 1.5 inches (1143 mm x 38 mm) contained inside a removable liner. The resultant sample volume is a maximum of 1300 mL. The MC® sampler may be used in either an open-tube or closed-point configuration. Although the MC® sampler can be used as an open-barrel sampler, the piston point is always used to prevent the collection of slough from the borehole sides.

Dual Tube Soil Sampling System

The Dual Tube 21 soil sampling system is a direct push system for collecting continuous core samples of unconsolidated materials from within a sealed outer casing of 2.125-inch (54 mm) OD probe rod. The samples are collected within a liner that is threaded onto the leading end of a string of 1.0-inch diameter probe rod. Collected samples have a volume of up to 800 mL in the form of a 1.125-inch x 48-inch (29 mm x 1219 mm) core. Use of this method allows for collection of continuous core inside a cased hole, minimizing or preventing cross-contamination between different intervals during sample collection. The outer casing is advanced, one core length at a time, with only the inner probe rod and core being removed and replaced between samples. If the sampling zone of interest begins at some depth below ground surface, a solid drive tip must be used to drive the dual tube assembly and core to its initial sample depth.

When the liners and associated sample are removed from the sample tubes, it is important to maintain the proper orientation of the sample, in order to ensure accurate logging.

Samples collected for geotechnical testing can be collected following the procedures discussed in Section 3.1.1.

3.1.4 Sonic Drilling Cores

Rotasonic drilling methods retrieve continuous core samples of solid and unconsolidated material. The drill rig has a dual line of drill pipe. The inner drill pipe attaches to a ten-foot long, 3.75" ID core barrel. The core barrel also attaches to a carbide-button drill bit. The outer line of drill pipe attaches to 5.875" – 6.5" OD carbide-button drill bits. The rotasonic method has two drilling options.

Sampling of shallow subsurface material (less than 30 feet below grade) can be performed using only the inner drill pipe and core barrel. Sampling runs of one-foot to thirty-feet can be performed depending on the type of material, degree of subsurface contamination, and sampling objectives. The samples are obtained by vibrating and rotating the core barrel to a desired depth, stopping the rotation and vibration, and then pulling the core barrel to the surface. The sample is then vibrated or hydraulically extracted into plastic sleeves or sample trays. A disadvantage of this option is the retrieval of sloughed material with the sample, which often results from sampling through the uncased hole. Therefore, the identification of sloughed material is important.

Sampling of shallow and deeper unconsolidated material and bedrock can be performed using a dual line of drill pipe. Sampling is performed by advancing the inner pipe ahead of the outer pipe to obtain representative samples. The hole is then cased by advancing the outer pipe to the sampled depth. Water or air is sometimes used remove the material between the inner and outer drill pipes.

In addition to retrieving continuous core samples, soil samples can be collected using other methods. Shelby tube or split-spoon samples can be collected in three ways: 1.) the sampler can be driven at the sampling depth using hydraulic pressure or vibration of the head; 2.) the sampler can be pressed into the core barrel after the desired sample has been retrieved; or 3.) the sampler can be pressed into the sample after is has been retrieved and vibrated into the sample container. The choice of the sampling method is dependent on the type of analyses to be performed.

When the liners and associated sample are removed from the sample cores, it is important to maintain the proper orientation of the sample, in order to ensure accurate logging.

Samples collected for geotechnical testing can be collected following the procedures discussed in Section 3.1.1.

3.1.5 Bulk Samples

Bulk samples are typically collected to perform laboratory compaction and California Bearing Ratio tests on. Samples are collected from auger cuttings during the drilling operation. The depth at which to collect the samples will be specified in the project documents. If a distinct subsurface strata break occurs over the sample interval for the bulk sample, contact the Project Engineer to determine if the sample should segregate the distinct strata.

Place the bulk sample material in an appropriate bucket or bag. At least 100-pounds is required for each sample specified. A jar used for SPT sampling should also be utilized to collect a smaller portion to be used for moisture testing.

Label both the bulk sample container and the moisture jar with the Project No., Boring No., depth of sample, and the date the sample was collected.

3.1.6 Rock Coring

The appropriate standard to follow for rock coring is ASTM – D 2113. The common sizes in use today for rock coring are NX, NQ, and NQ-2. The maximum length of the first core run on any borehole should generally not exceed 3-feet, unless otherwise specified by the Project Engineer. This is to ensure that the material being sampled is intact bedrock.

After the core sampler is retrieved from the borehole, the core should be placed in core boxes. The boxes should be labeled as shown below.

Box __ of __ Project No. _____
Location: _____
Boring No(s). _____ _____ _____ _ _____
Depth __ to __ __ to __ __ to __ __ to __
Date _____

Top of the Core Box Lid

Box __ of __ Project No. _____

Boring	Run	Depth	Penetration	Recovery	RQD	Date

Inside of Lid

Box __ of __ Project No. _____
Boring _____ _____ _____ _____

Right End of Box Looking at the Front of Box

The field representative should classify the rock sample and record the classification on the field boring log. Refer to the *Sample Description* section of this document for the appropriate classification system.

3.2 Sample Description

3.2.1 Soil

In general, the ASTM Standards to be used by field personnel classifying soils are D 2487 and D 2488. Slight modifications are utilized to customize the soil classification system to project specifc objectives. The soil classification is described by six discrete characteristics. These characteristics – constituents, density/consistency, color, moisture, plasticity (if plastic), and other – will yield the Unified Soil Classification System group and symbol. Determine the USCS Group Name and Group Symbol from Figures 1a and 2.

1. *Constituents*

Determine the particle size distribution. The particle size distribution is the percentage by weight of certain size soil particles that are included in the representative sample. Table 1 identifies the soil component and its corresponding size in millimeters (mm), inches, and U.S. Standard Sieve numbers.

TABLE 1 – PARTICLE SIZES

mm	INCHES	U.S. STANDARD SIEVE NO.	MATERIAL
> 304	> 12		BOULDER
305 – 76	12 – 3		COBBLE
76 – 19	3 – ¾		COARSE GRAVEL
19 – 4.76	¾ - 3/16		FINE GRAVEL
4.76 – 2.00	3/16 – 3/32	4 – 10	COARSE SAND
2.00 – 0.42	< 3/32	10 – 40	MEDIUM SAND
0.42 – 0.074		40 – 200	FINE SAND
0.074 – 0.005			SILT
< 0.005			CLAY

Reference: Department of the Navy, Facilities Engineering Command (NAVFAC) Design Manual (DM) – 7.1, Soil Mechanics, Chapter 1, Table 2.

There are a variety of methods to use in the field to identify the particle size distribution. The experienced engineer or technician will be able to perform this task visually, after much practice. A simple test to use is called the shake test. Select a representative sample of the soil and place a small amount of it in a clear sample jar so that is fills approximately 1-inch in the bottom of the jar. Measure the amount of total soil volume by marking it on the jar. Fill the jar with clean water, and shake vigorously for approximately 1-minute. Set the jar on a flat, level, steady surface free of

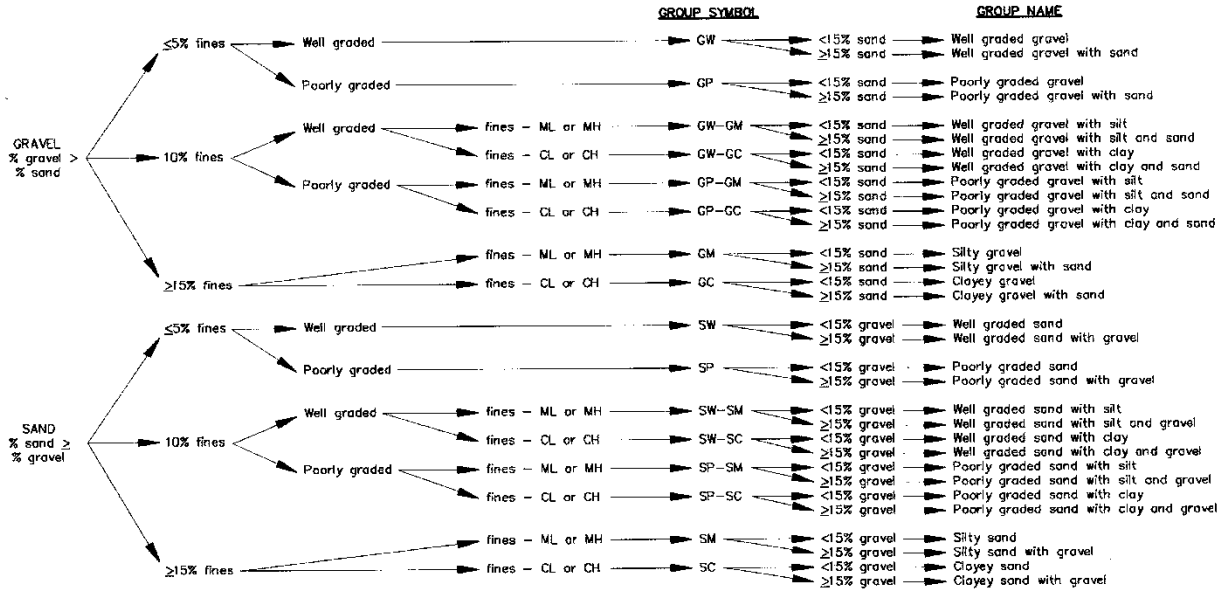
vibrations, and note the time. Most of the sand particles will fall to the bottom of the jar within 30 to 60 seconds. Most of the silt particles will fall to the bottom of the jar within 15-minutes. The remainder suspended in the water is clay. The field representative may use this test to estimate the grain size distribution, even though it is a volume-based test, not weight-based. There are many other test methods that are acceptable for use in determining the grain size distribution in the field.

In some cases, the field representative must characterize the gradation of coarse-grained soil (i.e. well-graded or gap-graded sands and gravels). A soil is well-graded if it has a wide range in grain size and substantial amount of each size. A soil is gap-graded if it has a wide range of size with intermediate sizes obviously missing. These descriptions apply to the USCS Group Symbols GW, GP, SW, and SP.

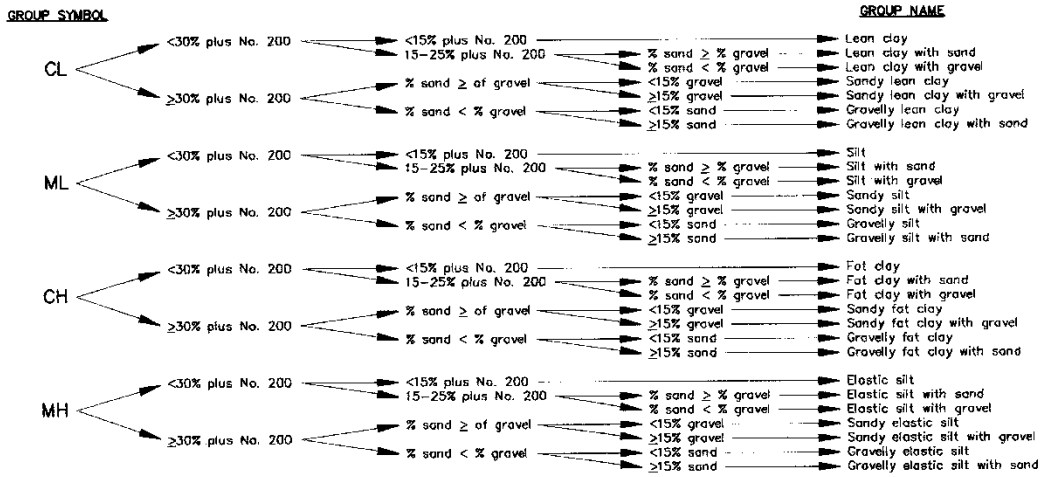
Since the human eye cannot distinguish particle sizes smaller than approximately 0.074 mm, other tests are necessary to differentiate silt and clay soils. These test classify the fine-grained soil (passing #200 sieve) based on their behavior. The simplest of these tests is the plastic thread test. To perform this test, take a representative sample from the soil, enough to create a ball approximately ½ -inch in diameter. Roll the ball on a hard surface with the palm of your hand into a thread shape. Continue rolling until the thread breaks, and note the diameter. Repeat by molding the broken thread pieces back together and re-rolling. Again, note the diameter of the thread. Also, note the relative toughness of the material during handling and rolling, particularly when the thread is approximately 1/8 –inch in diameter. Use Table 2 to identify the probable USCS Group Name.

Another common test is the dilatency test. To perform this test, take a small amount of soil from the representative sample and add enough water to make a soft, moist consistency. Smooth the soil pat in the palm of one hand and shake horizontally while striking the palm of the other hand. Note the reaction, then gently squeeze the sample in your hand and again note the reaction. If water appears on the surface during shaking and disappears quickly when squeezed, the reaction is rapid and the soil has low plasticity. If vigorous action is required to bring water to the surface and squeezing causes little change in appearance, the soil is of medium plasticity. High plasticity soil will have no visible reaction to shaking. Refer to Table 2 below for the probable USCS Group Name. A rapid reaction is indicative of silts, while a slow reaction is characteristic of clays. The water will travel through the silt particles relatively easily and the shaking causes the water to come to the surface.

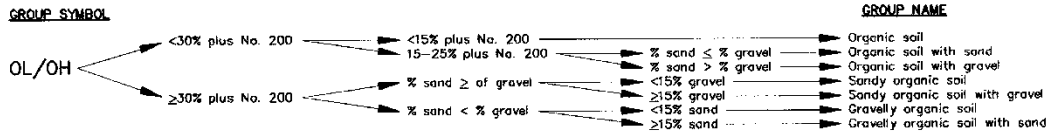
In order to differentiate between SILT (ML) and ELASTIC SILT (MH), and LEAN CLAY (CL) AND FAT CLAY (CH) one must know the liquid limit (LL) of the soil. The liquid limit is that moisture content where the soil becomes fluid. This property is very difficult to estimate in the field, and usually requires a laboratory test. It is only with practice and experience that the field representative will be able to recognize the approximate liquid limit of a sample. With this information, and the estimated laboratory plasticity index (PI), which is equal to the liquid limit minus the plastic limit (PL – moisture content at which the sample loses its plasticity), Figure 2 – Plasticity Chart can be utilized to determine the USCS Group Symbol.



Note – Percentages based on estimating amounts of fines, sand, and gravel to the nearest 5%.
FIG 2. Flow Chart for Identifying Coarse-Grained Soils (less than 50% fines)



Note – Percentages based on estimating amounts of fines, sand, and gravel to the nearest 5%.
FIG 1a. Flow Chart for Identifying Inorganic Fine-Grained Soils (50% or more fines)



Note – Percentages based on estimating amounts of fines, sand, and gravel to the nearest 5%.
FIG 1b. Flow Chart for Identifying Organic Fine-Grained Soils (50% or more fines)

FIGURE 1 – USCS FLOW CHART

Reference: American Society for Testing and Materials (ASTM) – D 2488

TABLE 2 - PLASTICITY

SMALLEST THREAD DIA ROLLED (in)	TOUGHNESS FO PLASTIC THREAD	DILATENCY REACTION	ESTIMATED LABORATORY PLASTICITY INDEX (PI)	PLASTICITY DESCRIPTION	PROBABLE USCS GROUP NAME (SYMBOL)
NONE	SOFT – WEAK	RAPID	0	NON-PLASTIC	SILT (ML)
¼	WEAK	RAPID	1 – 5	SLIGHT	SILT (ML) - ELASTIC SILT (MH)
1/8	MEDIUM	SLOW	5 –10	LOW	ELASTIC SILT (MH) – SILT (ML) – LEAN CLAY (CL)
1/16	MEDIUM STIFF	SLOW	10 – 20	MEDIUM	LEAN CLAY (CL)
1/32	STIFF	NONE	20 – 40	HIGH	LEAN CLAY (CL)
1/64	VERY STIFF	NONE	> 40	VERY HIGH	LEAN CLAY (CL) – FAT CLAY (CH)

Reference: American Society for Testing and Materials (ASTM) – D 2488, Table 12.

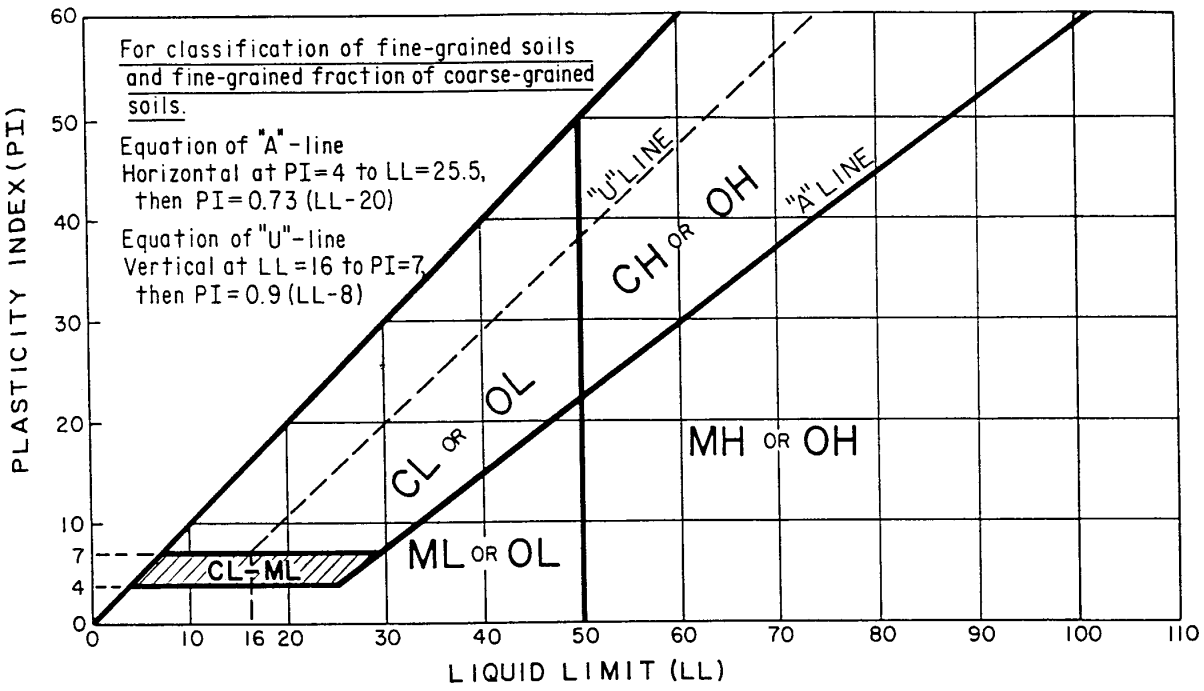


FIGURE 2 – PLASTICITY CHART

Reference: American Society for Testing and Materials (ASTM) – D 2487

2. Density/Consistency

The SPT N-values are used to estimate the relative density of granular soils (PI ≈ ≤ 10) and describe the consistency of fine-grained soils. Density can also be estimated by penetrating the soil with a ½ -inch diameter (#4) reinforcing bar pushed by hand. Table 3 should be used as a guide to determine a soil stratum's density.

TABLE 3 – DENSITY OF GRANULAR SOILS

SPT N-VALUE (bpf)	DESCRIPTION	RELATIVE DENSITY (D_r) (%)	FIELD TEST
0 – 4	VERY LOOSE	< 15	½-INCH (#4) BAR PENETRATED WITH LITTLE OR NO EFFORT BY HAND.
5 – 10	LOOSE	15 – 40	EASILY PENETRATED BY HAND. ROD WILL TAKE UP WITHIN 6 – 12-INCHES.
11 – 30	MEDIUM DENSE	40 – 70	DIFFICULTY IN PENETRATING BY HAND. ROD WILL TAKE UP WITHIN 3 – 6-INCHES
31 – 50	DENSE	70 – 85	ROD PENETRATED 12-INCHES DRIVEN WITH 5 POUND HAMMER.
> 50	VERY DENSE	85 – 100	ROD PENETRATED A FEW INCHES DRIVEN WITH 5 POUND HAMMER

Reference: NAVFAC DM – 7.1, Soil Mechanics, Chapter 1, Figure 1.

Fine-grained, or cohesive soils, are those soils with the majority of their soil particles passing the No. 200 sieve, and whose PI ≈ ≥ 10. The consistency of these soils is described using the SPT N-value, and the Pocket Penetrometer Test readings, to be described in a later section of this document. The consistency is related to the shear strength of the soil. The shear strength is frequently defined in terms of its unconfined compressive strength (Qu). The consistency for cohesive soils may also be estimated by comparing the effort that must be applied to the sample when squeezing between the fingers. Table 4 should be used as a guide to determine a soil stratum's consistency.

TABLE 4 – CONSISTENCY OF COHESIVE SOILS

SPT N-VALUE (bpf)	DESCRIPTION	UNCONFINED COMPRESSIVE STRENGTH (Q_u) (tsf)	FIELD TEST
< 2	VERY SOFT	< 0.25	EXTRUDED BETWEEN FINGERS WHEN SQUEEZED
2 – 4	SOFT	0.25 – 0.50	MOLDED BY LIGHT FINGER PRESSURE, EASILY PENETRATED
4 – 8	MEDIUM	0.50 – 1.00	MOLDED BY STRONG FINGER PRESSURE, WITH MODERATE EFFORT.
8 – 15	STIFF	1.00 – 2.00	READILY INDENTED BY THUMB, PENETRATED WITH GREAT EFFORT.
15 – 30	VERY STIFF	2.00 – 4.00	READILY INDENTED BY THUMBNAIL
> 30	HARD	> 4.00	INDENTED WITH DIFFICULTY BY THUMBNAIL

Reference: NAVFAC DM – 7.1, Soil Mechanics, Chapter 1, Table 4.

3. Color

The color used to describe a soil stratum should be indicative of a stratum change. There are references available such as a Munsel soil color chart to use to describe the color. The exact color is not as important as the identification of a stratum change. Use common color terms to describe the soil.

4. Moisture

The moisture content of soils is indicative of many factors. It may suggest a temporary or static ground water elevation, perched water, stratum change, or a transition to a confining layer. In cohesive soils, the moisture content influences the shear strength. The relative moisture content should be described using one of the three following terms.

DRY	SAMPLE IS AIR-DRY, NO VISIBLE MOISTURE
MOIST	VISIBLE MOISTURE, BUT NO FREE WATER
WET	FREE WATER VISIBLE, SATURATED

5. Plasticity

Refer to Table 2 to describe plasticity of the soil, *if* it is a cohesive soil

6. Other

Description pertinent to a thorough classification or characterization of the soil stratum may be included. Examples include mottling, weathering, or a quantity of a constituent not represented in the USCS Group Name. Use "Trace" for an amount less than 15%, if notable.

3.2.2 Rock

The format for classifying rock samples field personnel should use for this procedure is based on the Pennsylvania Department of Transportation (PA DOT) standard BC – 795. The ARM field representative should be familiar with the information contained in this standard, as it is a valuable reference.

Samples should be described with the following characteristics:

1. Rock Type – Examples include but are not limited to shale, sandstone, siltstone, limestone, diabase, etc.

2. Color – Indicative of stratum changes; use common terms.

3. Hardness – Describe the hardness according to Table 5.

4. Degree of Weathering – Describe according to Table 6.

5. Structural Features — Describe the bedding / lamination / foliation / flow-banding / cleavage thickness and relative dip of rock specimens according to Table 7.

6. Spacing of Joints / Faults / Fractures – Describe the thickness and relative dip of broken features of rock specimens according to Table 7.

Relative Dip (RD) is the angle of the features measured from horizontal.

TABLE 5 – HARDNESS CLASSIFICATION OF INTACT ROCK FROM CORE SPECIMENS

HARDNESS	FIELD TEST
EXTREMELY HARD	MANY BLOWS WITH GEOLOGIC HAMMER REQUIRED TO BREAK INTACT SPECIMEN
VERY HARD	HAND HELD SPECIMEN BREAKS WITH HAMMER END OF PICK UNDER MORE THAN ONE BLOW; LEAVES FAINT GROOVE WHEN SCRATCHED WITH KNIFE
HARD	CANNOT BE SCRAPED OR PEELED WITH KNIFE; HAND-HELD SPECIMEN CAN BE BROKEN WITH SINGLE MODERATE BLOW WITH PICK.
SOFT	CAN JUST BE SCRAPED OR PEELED WITH KNIFE; INDENTATIONS 1 – 3 MM SHOW IN SPECIMEN WITH MODERATE BLOW WITH PICK; SIMILAR TO CONCRETE.
VERY SOFT	MATERIAL CRUMBLES UNDER MODERATE BLOW WITH PICK AND CAN BE PEELED WITH KNIFE; CAN BE SCRATCHED WITH FINGERNAIL.

Reference: NAVFAC, DM-7.1, Soil Mechanics, Chapter 1, Table 9.

TABLE 6 – WEATHERING CLASSIFICATION

GRADE	DIAGNOSTIC FEATURES
FRESH	NO VISIBLE SIGN OF DECOMPOSITION OR DISCOLORATION; SPECIMEN RINGS UNDER HAMMER IMPACT.
SLIGHTLY WEATHERED	SLIGHT DISCOLORATION INWARDS FROM OPEN FRACTURES, OTHERWISE SIMILAR TO FRESH.
MODERATELY WEATHERED	DISCOLORATION THROUGHOUT; WEAKER MINERALS SUCH AS FELDSPAR DECOMPOSED; STRENGTH SOMEWHAT LESS THAN FRESH ROCK BUT CORES CANNOT BE BROKEN BY HAND OR SCRAPED WITH KNIFE; TEXTURE PRESERVED.
HIGHLY WEATHERED	MOST MINERALS SOMEWHAT DECOMPOSED; SPECIMENS CAN BE BROKEN BY HAND WITH EFFORT OR SHAVED WITH KNIFE; CORE STONES PRESENT IN ROCK MASS; TEXTURE BECOMING INDISTINCT BUT FABRIC PRESERVED.
COMPLETELY WEATHERED	MINERALS DECOMPOSED TO SOIL BUT FABRIC AND STRUCTURE PRESERVED (AKA SAPROLITE); SPECIMENS EASILY CRUMBLED OR PENETRATED.

Reference: NAVFAC, DM-7.1, Soil Mechanics, Chapter 1, Table 7.

TABLE 7 – DISCONTINUITY SPACING

DESCRIPTION FOR STRUCTURAL FEATURES	SPACING	DESCRIPTION FOR JOINTS, FAULTS, OTHER FEATURES
VERY THICKLY	> 6 FEET	VERY WIDELY
THICKLY	2 – 6 FEET	WIDELY
MEDIUM	8 – 24 INCHES	MEDIUM
THINLY	2 ½ - 8 INCHES	CLOSELY
VERY THINLY	¾ - 2 ½ INCHES	VERY CLOSELY
INTENSELY	¼ - ¾ INCHES	EXTREMELY CLOSE
VERY INTENSELY	< ¼ INCH	

Reference: NAVFAC, DM-7.1, Soil Mechanics, Chapter 1, Table 8.

The Rock Quality Designation (RQD) is a quantifiable description of the rock core specimens. RQD is applicable to NX, NQ, or NQ-2 size rock cores. Record the rock core size on the Field Boring Log. It is based on the total aggregate length of all core pieces greater than 4-inches long, measured along the core's axis, for a given core run. The field representative should read and be familiar with the procedure originally developed by Deere and Deere. Use the formula below to calculate RQD.

$$RQD = \frac{\sum LENGTH\ OF\ CORE\ PIECES \geq 4 INCHES}{TOTAL\ LENGTH\ OF\ CORE\ RUN} \times 100\%$$

The RQD pieces greater than 4 inches long are measured along the centerline axis of the core, and include pieces broken by mechanical means during the drilling process.

(Reference: ASTM – D 6032, Standard Test Method for Determining Rock Quality Designation (RQD) of Rock Core; "The Rock Quality Designation (RQD) Index in Practice," Deere and Deere, *Rock Classification Systems for Engineering Purposes*, ASTM STP 984, 1988.)

RQD should be recorded in the appropriate column on the Field Boring Log, a copy of which is included in this procedure.

In order to further assess the rock, drillability should be qualified. This can be done with descriptive terms. The field representative should also record the time required for a given length of core run and calculate a penetration per unit of time on the Field Boring Log.

Example: Limestone, gray, hard, slightly weathered, thickly bedded (RD=0°), widely spaced fractures (RD=40°).

Upon completion of a core box, the field representative shall take a photograph of the box showing the rock core and the data recorded on the inside of the lid.

3.2.3 Additional Logging Descriptors

1. Pocket Penetrometer Test Reading

As its name suggests, the pocket penetrometer is a small, hand-held device that estimates the unconfined compressive strength of a cohesive soil. The Pocket Penetrometer Test (PPT) should only be performed on cohesive soil samples. If the sample crumbles or breaks easily during testing, the PPT readings are invalid.

During testing, the field representative should fully support the soil sample in his or her hand, or in one side of the sampling spoon, and advance the pocket penetrometer at a slow but steady pace until it penetrates the sample ¼-inch as marked on the shaft of the penetrometer. Note or record the value read on the penetrometer. Several trials should be made for each sample and an average value used. Record the average for the corresponding sample on the field boring log.

2. Remarks

The field representative has the freest use of the Remarks column of the field boring log to provide supplementary information that is pertinent to thorough understanding of the subsurface conditions at the test boring location. Some items that should be considered to be included are:

- Surface conditions,
- Deviation from original location of test boring,
- Boring cave depth,
- Drilling resistance,
- Loss of drilling fluid,
- Backfill material,
- Soil strata origin (fill, residual, alluvial, colluvial, glacial till, etc.),
- Rock coring technique, if used, and
- Rock coring penetration per unit of time at a specified depth.
- Odor

- Effort should not be made to smell samples by placing near ones nose since this can result in unnecessary exposure to hazardous materials. However, odors should be noted if they are detected during the normal sampling procedures. Odors should be based upon such descriptors as those used in NIOSH "Pocket Guide to Chemical Hazards", e.g., "pungent", "sweet", etc., and should not indicate specific chemicals such as "BTEX" or "Phenol-like" odor.

- Presence of roots, root holes, organic material, anthropomorphic material, minerals, etc.
- NAPL presence characteristics, including sheen, etc.
- Reaction with HCl, if applicable.

Additionally, the following terms may be used to describe the soil structure.

TABLE 8 – TERMS USED TO DESCRIBE SOIL / ROCK STRUCTURE

TERM	DESCRIPTION
PARTING	PAPER THIN
SEAM	1/8 – 3-INCH THICK
LAYER	> 3-INCHES
SENSITIVE	PERTAINING TO COHESIVE SOILS THAT ARE SUBJECT TO APPRECIABLE LOSS OF STRENGTH WHEN REMOLDED.
INTERBEDDED	COMPOSED OF ALTERNATE LAYERS OF DIFFERENT SOIL TYPES
LAMINATED	COMPOSED OF THIN LAYERS OF VARYING COLOR AND TEXTURE
CALCAREOUS	CONTAINING APPRECIABLE QUANTITIES OF CALCIUM CARBONATE
SLICKENSIDED	HAVING INCLINED PLANES OF WEAKNESS THAT ARE SLICK AND GLOSSY IN APPEARANCE.

4 QUALITY ASSURANCE

The field representative will keep thorough notes of activities performed in the field as prescribed in the *Field Log Book* SOP. References to all boring logs and samples collected shall be maintained in the field log book along with any record of photographs taken. All photos should include a ruler or common object for scale. Photo orientation, location, and depth must be recorded in the field log book with notation.

Soil descriptions should be completed only by appropriately trained personnel. Descriptions should be reviewed by an experienced field geologist or engineer for content, format, and consistency. Edited boring logs should be reviewed by the original author to assure that content has not changed.

Soil Boring Log

Boring ID:

Project Name: Project Number: Client: Site: Borehole Location: Weather:	Date/Time Started: Date/Time Completed: Logged by: Checked by: Driller: Drill Rig Type/Method: Bit/Auger Size:	Northing (ft): Easting (ft): Surface Elevation (ft): Depth of Refusal (ft): Total Depth (ft): Depth to Water (ft):

Depth (ft):	Sample No:	Recovery (%):	PID (ppm):	PP reading (tsf):	Blow Count	DESCRIPTION	USCS	REMARKS
0								
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								

Soil Boring Log

Boring ID:

Depth (ft):	Sample No:	Recovery (%):	PID (ppm):	PP reading (tsf):	Blow Count	DESCRIPTION	USCS	REMARKS
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
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SOP No. 013
SOIL BORING METHODS
STANDARD OPERATING PROCEDURE

1 SCOPE

This Standard Operating Procedure (SOP) identifies the general guidelines for performing soil borings. The purpose of soil borings is to provide access to subsurface soils at specified locations and depths. Borings may be installed for the collection of geotechnical or hydrologic data; the installation of groundwater monitoring wells or in-situ remediation systems. This SOP is intended to provide a description of generally accepted industry practices for common methods of overburden drilling. The collection of subsurface soil samples is discussed in *SOP No. 009 Subsurface Soil Sampling*, the geologic logging of borings is covered in *SOP No. 012 Geologic Logging*.

No oils or grease will be used on equipment introduced into the boring (e.g., drill rods, casings, or sampling tools).

2 EQUIPMENT

Equipment may vary depending on specific project objectives and drilling methods to be employed. The following is a list of equipment that should, at a minimum, be present for the installation of soil borings:

Geologist

- Personal Protective Equipment (PPE)
  - Hard hat, steel- or composite-toed boots, gloves, hearing protection, safety googles.
  - A complete list of project-specific PPE should be available in the Health and Safety Plan (HASP) or Work Plan
- Boring logs and, if applicable, well completion forms
- Field logbook
- Site Plan with proposed boring/well locations and Work Plan
- Digital camera
- HASP
- Sampling equipment (e.g., buckets, trowels, spatulas, sample jars)
- Pocket penetrometer
- Equipment cleaning materials (e.g. decon solutions, paper towels, contractor bags, water)
- Any applicable laboratory sample containers, sample labels, chain-of-custody forms

- Insulated coolers with ice, when collecting samples requiring preservation by chilling
- If applicable, a photoionization detector (PID)
- Soil logging assistance tools (e.g., grain size charts, color charts, water)
- Measuring tapes and acoustic water level meters
- Indelible ink pens or markers
- Hand-held GPS unit

Drilling Contractor

- Drilling Equipment (dependent upon the drilling method employed)
- PPE (the Geologist or Project Manager should ensure that contractor PPE conforms with project-specific documentation and is used correctly by the contractor at all times)
- Well drilling supplies, as necessary (drilling mud)
- Decontamination Pad construction supplies
- Decontamination materials
- Well construction supplies, as necessary (screen, riser, well casing, well permits, sand pack, bentonite chips, bentonite, cement grout, water)
- Health and safety records required for working on-site
- Water supply
- Ancillary support vehicles
- Drilling logs
- Measuring tapes
- Tools
- Appropriate soil sampling equipment as specified in *SOP No. 009*

3 LOCATIONS

Borings should be collected at or as close as possible to the locations and depths provided in project work plan. Locations shall be confirmed via the use of a hand-held GPS unit and staked prior to drilling or excavating. Otherwise, sample locations shall be staked by a licensed surveyor prior to mobilization.

If required, the proposed locations may be adjusted in the field, based on site access, property boundaries, and surface obstructions. Sample locations where refusal is encountered prior to reaching target depths shall be relocated as close as reasonably possible to the original sample location, unless otherwise directed by the project manager. The location of the boring shall be recorded on the boring log via the use of a hand-held GPS unit or with survey coordinates, where available. The project manager shall be notified if a representative boring cannot be located near the locations provided in the project work plan.

3.1 Cautions

Underground utility locating will be conducted prior to all subsurface exploration. All public and privately owned utilities will be marked out on the ground surface prior to subsurface activities. No subsurface activities will be conducted within three (3) feet of a utility mark-out, and specific utility clearances should be confirmed with the utility owner prior to subsurface activities in the vicinity.

Prior to beginning excavation or drilling, underground utilities in the vicinity of the working areas shall be identified via one of the following three lines of evidence

- Contact the State One Call
- Obtain a detailed site utility plan drawn to scale, preferably an "as-built" plan
- Conduct a detailed visual site inspection

In the event that one or more of the above lines of evidence cannot be conducted, or if the accuracy of utility location is questionable, a minimum of one additional line of evidence will be utilized as appropriate or suitable to the conditions. Examples of additional lines of evidence include but are not limited to:

- Private utility locating service
- Research of state, county, municipal, or private utility records and maps including computer drawn maps or geographical information systems (GIS)
- Contact with the utility provider to obtain their utility location records
- Hand augering or digging
- Hydro-knife
- Air-knife
- Radio Frequency Detector (RFD)
- Ground Penetrating Radar (GPR)
- Any other method that may give ample evidence of the presence or location of subgrade utilities.

Overhead power lines also present risks and the following safe clearances must be maintain from them in accordance with American National Standards Institute (ANSI) Standard B30.5-1994, 5-3.4.5.

Power Line Voltage Phase to Phase (kV)	Minimum Safe Clearance (feet)
50 or below	10
51 to 200	15
201 to 350	20
351 to 500	25
501 to 750	35
751 to 1000	35

4 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to sampling. All requirements of the HASP should be maintained for the duration of the sampling. Any unforeseen hazards not specifically referenced in the HASP, identified by the sample shall be reported to the Project Manager prior to proceeding with field activities.

4.1 Site Reconnaissance

Selection of the proper drilling equipment for environmental and geotechnical sampling and monitoring well installation is a critical part of the field investigation. Project specific documentation including work plans, sampling and analysis plans, standard operating procedures, and quality assurance project plans should be reviewed by the Project Manager and Field Geologist prior to mobilization in order to determine the proper type of drilling technology and the tools and equipment required to meet project objectives. Drilling activities shall conform to all state regulations and the contractor or drilling subcontractor shall obtain all permits, applications, and other documents required by state or local authorities and the client. In addition, the following general guidelines should be thoroughly considered during the planning and implementation of all drilling operations:

- Review of background information for the investigation area. This should include identifying any contamination, the manner of release, and affected areas;
- Review of existing data on site geology and hydrogeology;
- Determination of potential and probable investigation derived wastes (IDW) and the methods required for the proper containment, disposal, and tracking of such IDW;
- Performing a site visit to determine field conditions, assess potential problems for a drill rig, and, if necessary, secure a potential water supply for drilling;
- Determine the volume of media required for requisite sampling;
- Determine if boreholes will be drilled through more than one water-bearing zone or aquifer, and what measures will be necessary to prevent cross-connection or cross-contamination of the zones and aquifers;
- Determine, to the extent possible, the level of contamination that will be encountered by each boring. Borings should be drilled in the order of no or low anticipated contamination and progress towards areas of increasing contamination. If practicable, upgradient areas with no anticipated contamination should be performed first; and
- Avoid using drilling mud, synthetic drilling fluids, petroleum or metal based pipe joint compounds, and other potential contaminants unless necessary. If their use is necessary, drilling fluids must not introduce or mask contaminants. Provide material safety data sheets

for all drilling fluids proposed for downhole use before field work and, if required determine procedures for containment and disposal of fluids. If it is necessary to add drilling mud to the borehole during drilling to stabilize the hole or control down-hole fluid losses, use only high-yield sodium bentonite clay, free of organic polymer additives.

4.2 Pre-Drilling Procedures

Working around drill rigs is dangerous. As a result, increased consciousness and oversight of drilling activities are critical, to reduce the risk of injury to workers involved with drilling. Safe work requires that good communication is maintained between the driller and the Field Geologist during drilling activities. Encourage the driller to notify the Field Geologist routinely of the depth(s) at which changes in drilling rates become evident and immediately of any other drilling observations that may indicate subsurface obstructions. At a minimum, the following activities should be conducted as part of the drilling program:

- Conduct a project kickoff meeting. Describe tasks to be conducted and a tentative schedule for the project at the beginning. As the project progresses, discuss the remaining tasks and revised schedule with the drill crew daily. Communicate progress and issues with the Project Manager.
- Hold a health and safety tailgate meeting to review the project- or site-specific HASP.
- Review and discuss with the driller the task specific activities identified in the drilling subcontractors Job Hazard Analysis (JHA).
- Wear proper PPE at all times.
- Visit the drilling locations with the driller prior to starting work to identify all potential site hazards and obstacles.
- Verify that the drilling locations have proper clearance from all underground and overhead utilities.
- Set up proper traffic controls if working in an area where traffic hazards are possible or anticipated.
- Establish any necessary exclusion zones using barriers, caution tape, or other methods to prevent unauthorized access to the drilling location.
- Inspect the drill rig for leaking lines or other hazards. No fluids should leak from the rig.
- Identify the locations of the fire extinguisher(s) and first aid kit(s), and verify that they are readily available for use.
- Maintain good housekeeping on and around the rig at all times.
- Establish a staging area for storing IDW and decontaminating augers, rods, and/or sampling equipment.
- Establish a core logging and sample collection area at a safe location within sight of the drill rig.

- Place sampling equipment and soil recovered from the subsurface on plastic sheeting or similar dedicated material to avoid potentially contaminating the ground surface.
- Carefully log any downtime that occurs due to subcontractor equipment failure, weather, site-access, or other issues, and any time where the field geologist is causing a significant delay in field activities in the field log book.

4.3 Drilling Equipment Cleaning and Decontamination

Prior to mobilization, the drill rig and all associated equipment should be thoroughly cleaned to remove all oil, grease, mud, etc. Any equipment that is not required at the site should be removed from the rig prior to entering the site. To the greatest extent possible, drilling should proceed from the least to most contaminated sections of the work site.

Before drilling each boring, all the down-the-hole drill equipment, the rig, and other equipment (as necessary) should be steam cleaned, or cleaned using high-pressure hot water, and rinsed with pressurized potable water to minimize cross contamination, if appropriate. Special attention should be given to the thread section of the casings and to the drill rods. Additional cleaning may be necessary during the drilling of individual holes to minimize the carrying of contaminated materials from shallow to deeper strata by contaminated equipment.

Equipment with porous surfaces, such as rope, cloth hoses, and wooden blocks or tool handles cannot be thoroughly decontaminated. These should be disposed of properly at appropriate intervals. These intervals may be the duration of drilling at the site, between individual wells, or between stages of drilling a single well, depending upon characteristics of the tools, site contamination, and other considerations.

Cleaned equipment should not be handled with soiled gloves. Surgical gloves, new clean cotton work gloves, or other appropriate gloves should be used and disposed of when even slightly soiled. The use of new painted drill bits and tools should be avoided since paint chips will likely be introduced to the monitoring system.

All drilling equipment should be steam cleaned or cleaned using high-pressure hot water, if appropriate, at completion of the project to ensure that no contamination is transported from the sampling site.

IDW should be handled in accordance with *SOP No. 005 Investigation-Derived Wastes*.

4.4 Drilling Methods

The following presents a description of some common drilling methods utilized for overburden drilling. The drilling method will be selected based upon the physical properties of the subsurface materials and project specific objectives.

4.4.1 Hollow Stem Auger Methods

Hollow stem auger drilling is a form of rotating auger drilling, consisting of continuous-casing, segmented auger sections with screw-flights that are rotated into the subsurface under downward pressure. The auger section is typically equipped with a drill bit and cutting teeth. Drill cuttings are brought to the surface by a conveyor action created by rotating screw flights and the drill bit. The auger sections maintain borehole stability, even in unconsolidated material. Generally, hollow steam auger drilling is limited to depths less than 100 feet where lithology is unconsolidated. Multiple auger sections are connected in series to create a "drill string" with clamping pins or screw fittings.

In-situ soils may be sampled through the center of the hollow stem auger drill stem. An advantage of this type of drilling is that auger sections can be left in place to hold the borehole open and reduce slough in unconsolidated soils. If installing a monitoring well, the well casing, filter pack and seal are installed inside the auger. The auger is removed slightly ahead of backfilling as filter pack, bentonite and grout are added.

Hollow stem augers are specified by the internal diameter of the hollow stem, rather than the size of the hole they drill. Augers with a minimum inner diameter of 4.25" should be used to install 2" diameter monitoring wells, to give clearance around the well for filter pack sand and bentonite seals. If a 4" diameter monitoring well is required, the inner auger diameter must be 6" to 8".

Auger flights and sampling equipment (e.g., split spoon samplers, shelby tubes) should be pre-cleaned and decontaminated prior to boring.

4.4.2 Direct Push

Direct push systems involve a category of drilling equipment that hydraulically pushes or drives small-diameter, hollow steel rods into the subsurface without rotation. Some drill rigs may be "combo rigs," capable of conducting both direct push and rotating hollow stem auger drilling operations. Direct push drilling uses a combination of a hydraulically powered percussion hammer, a downward hydraulic push, and the weight of the vehicle on which the system is mounted to drive rods into the subsurface by laterally displacing soil to make a path for the sampler, so no cuttings are generated. Direct push drilling is commonly used for shallow applications; however, depending on the lithographic conditions, it may be used as deep as 120 feet.

Direct push technology is typically limited to unconsolidated formations that are relatively free of cobbles or boulders. Refusal may occur if there are too many cobbles, boulders, consolidated formation materials, or anthropomorphic debris. However, since direct push drilling is relatively fast, refusal at a desired location may be mitigated by abandoning the hole, moving to a nearby location, and re-drilling.

Direct push boreholes generally cannot be sampled deeper than the water table because unconsolidated materials cave in once the drive rods are removed. However, caving may be

mitigated by advancing a casing with an inner drill rod used for sampling, allowing for sampling and well installation far below the water table. Outside diameters of samplers and boring tools generally range from 0.75" to 3.5". If installation of monitoring wells is planned, the inside diameter of the boring should typically ranges from 1.5" to 3.5" (for 1" to 2" wells).

Direct push technologies offer the following advantages over conventional drilling methods:

- Minimal ground disturbance, with a small diameter boring that is easy to abandon;
- No cuttings, i.e., minimal Investigation Derived Wastes (IDW) generation;
- Faster boring advancement;
- Faster monitoring well installation if small diameter wells (0.75" to 1" diameter) with pre-packed screens are installed.

Boreholes should be completed using pre-cleaned and decontaminated (or disposable) drive points, rods, and sampling equipment.

4.4.3 Mud Rotary Drilling

During fluid-rotary drilling, the borehole is drilled by a rotating bit; cuttings are removed by continuous circulation of a drilling fluid as the bit penetrates the formation. The bit is attached to a string of drill rods that transmits the rotating action and drilling fluid from the rig to the bit.

There are a variety of fluids that can be used in conjunction with this drilling method. The usual drilling fluid is water or water mixed with bentonite (referred to as "mud-rotary"). Under some geologic conditions, it may be necessary to add other compounds to the drilling fluid to increase the fluid weight or viscosity. These additions may include inorganic compounds such as barite or organic polymers. For monitoring wells constructed to sample groundwater quality, the use of any organic polymers in the drilling fluid should be avoided and inorganic additions made only if they will not interfere with the groundwater sampling protocol. The Project Manager should be consulted before a drilling fluid other than clear water is to be used. The decision as to whether drilling fluid additives should be used should be based on consultation with the client and review of any guidance documents used by the lead regulatory agency, if appropriate. Even if an agency is not currently involved with the project, it may be advisable to utilize their method of preference so environmental data and analytical results cannot be questioned at a later date.

There are two general types of fluid-rotary drilling methods: direct circulation rotary drilling and reverse circulation rotary drilling. In direct circulation rotary drilling, the drilling fluid is circulated down through the drill rods, out the bit, and up the annular space to the settling pit at the surface. In the reverse circulation rotary method, the drilling fluid and cuttings move down the annulus and upward inside the drill rod to be discharged into the settling pit. Upon boring completion, clean water should be circulated through the system to remove residual additives from the borehole and facilitate subsequent well development.

Advantages to rotary drilling methods include:

- The ability to advance a hole in most formations at a relatively quick pace;
- Split-barrel samples, Shelby tubes, and rock cores can be obtained;
- Casing may not be needed because the drilling fluids may keep the borehole open;
- They are relatively common methods that are used by water well drillers in most areas; and
- The open hole can be geophysically logged.

Disadvantages to this method include:

- Formation logging is difficult if split-barrel samples are not taken;
- Drilling fluid reduces formation permeability to some degree, may circulate contaminants, or alter groundwater quality in the vicinity of the well;
- Limited or no information on depth to water and/or occurrence of water-bearing zones is obtainable while drilling;
- Development techniques for wells may be more extensive when compared to other drilling methods;
- Drill rigs are usually large and heavy and need proper access;
- Federal and state regulatory agencies may prohibit the use of this method for some applications because of the addition of fluids in the hole; and
- Potable water is required for mixing drill fluids. This water should be sampled and the water source should remain the same throughout the program. This method may require a large volume of water. The availability of a potable water source should always be considered in the selection of this method.

4.4.4 Air Rotary Drilling

This method is similar to fluid-rotary drilling, except that compressed air is used to cool the drill bit and remove cuttings. Two drilling methods that use air as the primary drilling fluid are direct air-rotary and down-the-hole air hammer. Applications of air-rotary methods include:

- Rapid drilling of semi-consolidated and consolidated rock;
- Good quality/reliable formation samples (particularly if small quantities of water and surfactant are used);
- Equipment generally available;
- Allows easy and quick identification of lithologic changes;
- Allows identification of most water-bearing zones; and
- Allows estimation of yields in strong water-producing zones with short "down time".

Limitations of this method include the following:

- Surface casing is frequently required to protect the top of the hole from washout and collapse;
- Its use is restricted to semi-consolidated and consolidated formations;
- Samples are reliable but due to small size are difficult to interpret;
- Drying effect of the air may mask low yield water producing zones;
- Air stream may require filtration to prevent introduction of contaminants from the air compressor; and
- The injected air may modify the chemical or biological conditions of the aquifer in the immediate vicinity of the borehole.

4.4.1 Rotosonic Drilling

Rotosonic is a core drilling method that employs simultaneous high frequency vibration and low speed rotational motion along with downward pressure to advance the core barrel without use of drilling fluid or air. The core barrel can generally advance from five to twenty feet at one time, depending on the length of the core barrel. The drill cuttings are brought to the surface by removal of the entire core barrel from the borehole and the cuttings are vibrated out of the barrel. If required for logging purposes, the cuttings are collected in plastic sleeves. An outer casing is generally washed-down with water to stabilize the borehole from collapse and heaving sand. The outer casing prevents cross-contamination and formation mixing. The advantage of rotosonic core drilling is that no drilling fluids or muds are required to bring the cuttings to the surface and the aquifer is less likely to be contaminated by the drilling method. Split-barrel and Shelby tube samples can be collected using Rotosonic methods.

4.5 Heaving and Flowing Soils

The presence of heaving and flowing soils within the deeper saturated zone is a known issue at the Sparrows Point Terminal Site. When encountered, use appropriate drilling techniques to minimize potential impacts; these includes using drilling fluids or a drill-stem plug. Minimize the use of drilling fluids if possible. However, when necessary, it is permissible to add potable water from a documented, clean source and/or drilling mud to the borehole to control heaving and flowing soils as long as identification of the saturated zones during drilling is not compromised and the drilling fluid can be removed during development so that representative water levels can be obtained. All drilling fluid volume added to a borehole must be developed from the well. If potable water is added to the borehole, develop an equal volume of water from the borehole, in addition to the standard well development volume. If a drill-stem plug is used, slowly release the plug from the end of the drill-string while at total borehole depth.

5 QUALITY ASSURANCE

All field activities shall follow guidelines presented in the project specific documents. Any changes required based on conditions encountered in the field are to be documented in the field logbook and shall be approved by the project manager.

Logging of soil borings shall be consistent with the requirements of *SOP No. 012 Geologic Logging.* Soil sampling for the purposes of geotechnical and analytical testing shall following the requirements of *SOP No. 012* and *SOP No. 009 Subsurface Soil Sampling.* Monitoring Well Construction shall be consistent with the requirements of *SOP No. 014 Monitoring Well Construction in Unconsolidated Formations.*

SOP No. 014
MONITORING WELL CONSTRUCTION IN UNCONSOLIDATED FORMATIONS STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

This Standard Operating Procedure (SOP) provides procedures for the proper construction of groundwater monitoring wells in unconsolidated formations. Groundwater extraction, or pumping test wells, will be constructed using the same general procedures.

Monitoring wells are used for many purposes: collection of groundwater for chemical analysis; measurement of groundwater levels; detection of free-phase constituents; and aquifer testing. The specific purpose for which the well was constructed, the regulatory framework applicable to the well construction, the expected useful life of the well, and other factors may have significant bearing on the construction technique employed. However, all wells, regardless of intended purpose, should be constructed to minimum standards to ensure the following:

- Good hydraulic connection is established between the well and the water-bearing zone of interest;
- Water from separate zones or aquifers are not interconnected, and well construction activities do not facilitate cross-contamination;
- Well construction activities do not alter the chemical characteristics of the aquifer;
- The well is properly sealed to prevent entry of surface water; and
- The well is properly identified.

In general, the monitoring well construction will adhere to the SOP listed below. However, modification to the SOP may occasionally be required based on actual conditions encountered in the field. Justification of field modifications can be provided, as needed.

2 EQUIPMENT

Equipment and materials used for drilling and constructing monitoring wells in unconsolidated formations will depend upon the chosen drilling and subsurface sampling methods, and well design. Based upon the chosen methods, the drilling subcontractor will be responsible for providing a

drilling rig, support equipment, and trained drilling crew capable of performing the requested drilling and installation activities. The qualified driller will typically know, based on experience, what equipment will be required for specific situations. It is necessary, therefore, to provide the driller with as much information as possible regarding the requirements and objectives for the drilling and monitoring well installation, as well as the anticipated subsurface conditions.

Besides the general equipment necessary to drill the boring, well installation equipment will likely include the following:

- Various pumps, e.g., mud, trash, grout, etc.
- Various hoses for fluids and air
- Casing lifts (cables, clamps, hoists)
- Portable water tank, transfer lines, and pump (as needed)
- Cutting torch and welder
- Grout and slurry mixing machines
- Tremie lines and drop pipes

The driller will also obtain the required materials for well installations. Material specifications will be the responsibility of the overseeing field personnel or project manager. The specifications are dependent upon anticipated subsurface conditions. The process by which the proper materials are selected is presented in the following section.

Well construction materials typically will include the following:

- Temporary casing
- Well screen
- Riser pipe (to extend from the screen to the surface)
- Centralizers
- Sand and/or gravel pack
- Sealing materials (bentonite chip, powders, etc.)
- Grouting materials
- Protective steel casings, manholes, and/or flush-mount caps
- Compression caps
- Locks and keys
- Concrete for pad construction

In addition to the equipment and material needs of the driller, the field manager overseeing the monitoring well construction activities will require particular items to assist in documenting construction activities. Equipment and materials likely to be used by oversight personnel may include:

- Field logbook and indelible ink pens
- Personal protective equipment (PPE) as prescribed in the Health and Safety Plan (HASP)
- Digital camera
- Mud balance (for grout density measurements)
- Weighted tape for measuring borehole depths and well construction material placement
- Tape measure and/or ruler
- Water-level and/or interface probe
- Multi-parameter meter to measure pH, temperature, specific conductance, and turbidity during well development.

3 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to monitoring well installation. All requirements of the HASP should be maintained for the duration of the installation. Any unforeseen hazards not specifically referenced in the HASP, identified by field personnel shall be reported to the Project Manager prior to proceeding with field activities.

3.1 Borehole Installation

Drilling methods and borehole construction practices are discussed in *SOP No. 013 – Soil Boring Methods*. When a boring may be used for the construction of a monitoring well, the drill should use a high-pressure, hot water, power washer, i.e., steam cleaner to clean all bits, pipe augers, and any other drilling or sampling tools that may be used in the advance of the borehole (*SOP No. 016 Equipment Decontamination*). No grease or other machine lubricants should be used during the well construction (some regulatory agencies will allow selected lubricants with prior approval). The borehole must be of suitable diameter (the diameter of the boring should be at least four inches greater than the outside diameter of the well pipe for permanent monitoring wells) and depth for the monitoring well planned. If the boring extends more than a few feet below the planned depth of the monitoring well, the lower portion of the boring should be sealed with a structurally suitable bentonite seal (i.e. bentonite pellets) to provide a base for the well. Cement grouts should not be used to seal borings because of possible effects on groundwater chemistry.

3.2 Well Casing and Screen

The well casing (riser pipe) and screen for most permanent monitoring well installations will be two- or four-inches in diameter. Two-inch diameter wells are generally used because:

- They require smaller borehole diameters, which reduce drilling costs;
- The smaller diameter reduces the volume of cuttings, which may have to be disposed;
- Construction material costs are lower; and
- The volume of water that must be purged during well sampling is less.

A four-inch diameter well may be preferred when wells are built to collect groundwater samples from silt and/or clay sediments. Wells screened in these sediments tend to produce turbid samples. Increasing the well screen diameter reduces the groundwater entrance velocity, which helps to reduce the turbidity of the samples. Using "wire wrapped" as opposed to slotted screens will also help to reduce sample turbidity for the same reason. Increasing the well diameter also reduces the surge energy that reaches the formation when a snug fitting bailer is dropped into the well to collect samples. The selection of well diameter for low yielding silt and/or clay aquifers should take into account the volume of water to be purged from the well during sampling. Costs associated with disposal of purge water and slow labor requirements for purging/sampling wells recharge wells may negate the advantage of installing a larger diameter well. A four-inch diameter well may also be preferred when wells are built to collect groundwater samples from sand and/or gravel material. Wells screened in highly transmissive aquifers are occasionally difficult to fully develop without pumping. For this reason, well diameters may be increased to accommodate a submersible pump. Deeper wells may also require a submersible pump to efficiently lift groundwater during development and purging.

For most groundwater monitoring applications, polyvinyl chloride (PVC) is a suitable material for both well casing and screens. It is readily available, is low in cost, and generally unaffected by the chemistry of most groundwaters. However, when sampling for chlorinated organic compounds, PVC pipe and screens may be unacceptable. Also, some phase-separate liquids, including some petroleum products or high concentrations of some solvents, may have an adverse effect on the integrity of PVC pipe and screens. The material supplier can usually provide information regarding material incompatibilities if the nature and concentration of the contaminants are known. Some regulatory agencies require specific well construction materials for monitoring well use. Wells intended for the collection of monitoring data subject to regulatory review must be constructed of materials and in a manner approved by the designated agency.

Stainless steel pipe and screens are usually an acceptable alternative when PVC cannot be used. Stainless steel is more expensive than PVC and will usually require one or two weeks lead time to assure delivery of materials.

In some cases, where metals are a contaminant of concern, stainless steel is unacceptable and PVC or other well screen and casing materials (e.g., Teflon®) should be used. Combinations of materials may also be used in some cases (for example, using stainless steel or Teflon® for those portions of the well below the water table and PVC through the unsaturated zone). Attention must be given to the joints of these hybrid wells. To eliminate corrosion where dissimilar construction materials connect (for example, if a well is constructed of stainless and black steel pipe) nonconductive joint rings may be necessary at the fittings. The material supplier can usually provide information regarding material incompatibilities. Terminating the well with a section of PVC pipe may also make the well completion easier to accomplish, especially where the top of the well pipe must be cut to fit inside a surface-mounted well cover.

Threaded well casing and screens shall be used for monitoring well applications. Glued joints shall not be used for any monitoring well construction. The threaded joints typically include an O-ring that, when properly installed, assures a leak-tight joint. Threaded joints also reduce the chance of introducing organic constituents to the well, which may occur when solvents are used to weld PVC pipe. The threaded joints also provide a smooth interior, which reduces the likelihood that sampling tools or measuring tapes will become hung up inside the well. Teflon® tape may be used to lubricate threads, and clean water or hydrated bentonite may be used to lubricate O-rings.

The well casing and screens should always be new material. Proper storage, both at the site and before delivery, is required to assure the pipe is clean.

A threaded, slip-over or an expanding-type well cap should top each well. The well cap should have a small hole drilled through it to maintain atmospheric pressure at all times. This allows wells to recover more quickly to static conditions after sampling and will help prevent the cap from sticking due to a low-pressure condition in the well. A threaded plug should be installed in the bottom of the well. A small hole should be drilled through the plug to allow the well to completely drain should the water table drop below the bottom of the well, if applicable.

Centralizers should be used depending upon the depth of the well to assure the well casing is centered in the borehole, unless the well is installed through hollow stem augers. Hollow stem augers will keep the well reasonably centered without the use of centralizers. One centralizer should be placed at the bottom of the well screen and another approximately 10 feet below the top of the well. Additional centralizers should be placed at 25-foot intervals.

Well screen slot size should be selected based on the grain size of the formation to be sampled. The well screen should retain 90 percent of the formation sand for naturally developed wells or 90 percent of the filter-pack sand. If a grain size distribution is not available for the formation, the following guideline (Gass, 1988) should be followed.

Anticipated Strata	*Well Screen Size (inches)*	*Filter Pack Material (Approximate Range of Standard United States Sieve Sizes)*
Sand and gravel	0.030	20 to 4
Silt and sand	0.020	30 to 8
Clay and silt	0.010	50 to 16

3.3 Annulus Filling

Naturally developing a monitoring well (allowing the natural formation sands to cave around the well screen) is acceptable when the grain size distribution of the formation is known and the well screen was properly selected to retain the formation sand. However, this information is not usually available before the well is constructed. Consequently, most monitoring wells will be filter packed.

Filter pack sand should be clean, well-rounded, uniformly sized (uniformity coefficient of 3.0 or less) silica sand, free of organic matter and carbonate grains. The filter pack should be placed from the bottom of the well to no less than 1 foot nor more than 2 feet above the well screen. A 0.5-foot thick layer of very fine sand (sand blotter) should be placed at the top of the filter pack to separate the filter pack from the overlying bentonite seal. If using mud rotary drilling methods, the filter pack sand should be washed into place through a tremie pipe with water from a potable source.

A bentonite seal should be placed in the well above the filter pack sand. Bentonite pellets or chips may be used if they are installed below the water table and do not have to free fall through more than approximately 15 feet of water. Where the bentonite is installed through more than 15 feet of water, the bentonite should be hydrated and emplaced as a slurry under pressure through a tremie pipe. The slurry should consist of approximately 15 pounds of powdered bentonite to 7 gallons of portable water. The tremie pipe should have a deflector at the bottom to prevent the grout from being jetted into the filter pack sand.

The bentonite seal should extend from the top of the sand blotter up the annular space to the water table surface for a minimum of 3 feet. A second 0.5-foot thick sand blotter should top the bentonite seal. The annular space above the water table should be filled to within 3 feet of the surface with a cement/bentonite grout consisting of 2 to 5 pounds of powdered bentonite per bag of Portland cement mixed with 5 to 6 gallons of potable water. The cement/bentonite grout should be properly mixed using appropriate grouting equipment. The cement/bentonite grout should be tremied into place from the bottom of the annulus to the top using a grout pump. The tremie pipe should have a deflector at the bottom to prevent jetting of the grout into the bentonite seal.

Where the concentration of total dissolved solids in the groundwater is high (greater than approximately 500 parts per million), the chloride concentration is high, or when substantial thickness of phase-separated liquids are present, neither bentonite nor cement/bentonite grouts may

be suitable. Under these cases, the grouting material must be selected based on the specific characteristics present at the site.

The upper five feet of the annulus (or to the top of the bentonite seal when it terminates at depth less than five feet) should be filled with concrete. This portion of the annulus seal needs the structural strength of concrete to protect the casing and the well cover. The concrete should extend below the frost depth. The concrete should be no more than a few inches larger in diameter than the well borehole. This will prevent frost action from lifting the well. The top of the concrete should slope away from the well to direct rain water away. Where a concrete apron surrounding the well is desired or required by regulation, it should be constructed with a joint around the concrete that fills the top of the annulus to assure separation of the well from the apron.

3.4 Well Covers and Surface Finishing

A well cover should be set in the concrete at least three feet below the ground surface and extend one to two inches above the well pipe. The diameter of the well cover should be sufficient to allow room to remove the well cap with gloved hands. The well cover should have a locking, hinged lid that prevents the entrance of rain water. A small hole should be drilled in the side of the well cover approximately six inches above the ground surface to allow moisture to drain from the well cover, if applicable. The space between the well cover and the well pipe should be filled with coarse sand or fine gravel.

Alternately, the well may terminate in a specifically-built surface mount well cover. The surface mount well cover should never be used when the ground surface is low and storm water could pond over the well. When the existing surface is low and a flush-mounted well is designed, the surface should be regraded to prevent water from standing over the well. In paved parking lots or driveways, a small mound two to three inches high sloping away from the well may be sufficient to divert storm runoff away from the well opening.

Permanent labels should be affixed on both the inside and outside of the well cover lid. The label should include a unique well identification code and the elevation of the water level measuring point. The label may also include the date the well was drilled. A notch should be cut or filed in the top of the well pipe to mark the water level measuring point.

3.5 Grouting Techniques

There are several methods for monitoring well grouting. In determining the specific grouting requirements for a monitoring well, considerations must be given to existing subsurface geologic and groundwater conditions. The most effective grouting method should be selected by the site hydrogeologist based on the particular site conditions. Selection of the grouting technique and material may be limited by state or local regulations. Consultation with appropriate agencies prior to beginning grouting activities is advisable. Site-specific methodologies should be stipulated in the project work plan.

Prior to grouting, the annular space should always be flushed to assure that the space is open and able receive the sealing material. This is performed by circulating water or other drilling fluid in the annular space. Grouting should be performed in one continuous operation in which the annular space is filled. Grout containing cement should be placed entirely before the occurrence of the initial set. It is essential that the grout always be introduced at the bottom of the space being grouted such that positive displacement of any water in the annular space occurs.

The grout may be forced into the annular space by suitable pumps or by air or water pressure. Under certain conditions (*i.e.*, when no water exists in the annular space), placement by gravity is practical and satisfactory.

The following sealing and grouting procedure is recommended for most monitoring wells. Following placement of the filter pack, a 2-foot bentonite seal should be placed above the filter pack. Granular bentonite, bentonite pellets, or bentonite chips are suitable for this application. For monitoring wells that are less than 30 feet deep, the bentonite may be dropped directly down the borehole within the annular space. This should be performed gradually and uniformly in order to prevent bridging. In addition, a tamping device should be used to prevent bridging. For monitoring wells that are greater than 30 feet deep, bentonite should be delivered using a tremie pipe. If a bentonite seal is installed in the unsaturated zone, granular bentonite should be used, gradually hydrated with potable water, and allowed to cure prior to grouting.

Grouting of the remaining annular space should be performed using a tremie pipe with side discharge ports, a grout pump, and the neat cement grout or bentonite/cement grout in slurry form. The grout slurry should be pumped to the bottom of the borehole through the tremie pipe which should be kept full of grout for the duration of the procedure. The tremie pipe should be raised slowly as the annular space fills with grout. As the tremie pipe is raised, the discharge ports should be kept submerged within the grout until the desired zone is completely grouted. An annular space of at least 2 inches between the borehole wall and the well casing should exist, and the minimum inside diameter of the tremie pipe should be 1.5 inches.

3.6 Direct Push Methods for Monitoring Well Installation

A variety of Direct Push methods are available for installing temporary or permanent monitoring wells. The two main installation methods used are exposed-screen and protected-screen wells. These methods are discussed in detail in ASTM D-6724 and D-6725 (ASTM, 2003a and 2003b) and are summarized here.

3.6.1 Exposed-Screen Well Installation Methods

With exposed-screen well installation methods, the well casing and screen are driven to the target depth using a single string of rods. Because the screen is exposed to formation materials while it is advanced, proper well development is important to remove soil from screen slots. This method is not recommended for installing well screens within or beneath contaminated zones because drag-

down of contaminants with the screen may cross-contaminate sampling zones and make acquisition of samples representative of the target zone impossible. Exposed-screen well installation methods should only be used in upgradient areas that are known to be uncontaminated. Also, some states prohibit allowing the formation to collapse around a well screen in the construction of a monitoring well. Therefore, state regulations should be consulted before selecting exposed-screen techniques.

In one type of exposed-screen installation, the PVC well screen and casing are assembled and placed around a shaft of a drive rod connected to a metal drive tip. The casing and screen, which rest on top of the drive tip, are advanced to the target depth by driving the rod to avoid placing pressure on the screen. The drive tip slightly enlarges the hole to reduce friction between the formation and the well screen and casing, and remains in the hole plugging the bottom of the screen. The filter pack surrounding the well screen commonly is derived from formation materials that are allowed to collapse around the screen. Rigorous well development improves the hydraulic connection between the screen and the formation and generally is necessary to remove formation fines and the effects of well installation, which may include borehole smearing or the compaction of formation materials. Due to the very small annulus (if any) that surrounds a well, constructed using the exposed-screen method, it is not generally possible to introduce a filter pack or annular seal from the surface.

Exposed-screen methods also can be used to install well points (simple wells used for rapid collection of water level data, groundwater samples, and hydraulic test data in shallow unconfined aquifers). Well points are generally constructed of slotted steel pipe or continuous-wrap, wire-wound, steel screens with a tapered tip on the bottom. They can be driven into unconsolidated formations and used for either point-in-time sampling and decommissioned after the sample is collected, or left in place for the duration of the sampling program possibly requiring the installation of a seal to prevent infiltration of water from the ground surface to the screened interval.

The optimum conditions for well point installations are shallow sandy materials. Predominantly fine-grained materials such as silt or clay can plug the screen slots as the well point is advanced. Because well points are driven directly into the ground with little or no annular space, the formation materials are allowed to collapse around the screen, and the well point needs to be developed to prepare it for sampling.

3.6.2 Protected-Screen Well Installation Methods

When installing a protected-screen well, the well casing and screen are either advanced within or lowered into a protective outer drive rod that has already been driven to the target depth. Once the well casing and screen are in place, the drive rod is removed. Alternatively, the casing, screen, and a retractable shield may be driven simultaneously to the target depth. Once in place, the screen is exposed and the entire unit remains in the ground. If there is sufficient clearance between the inside of the drive rod and the outside of the well casing and screen, a filter pack and annular seal may be installed by tremie from the surface as the drive casing is removed from the hole. Several filter packing and annular sealing approaches are available, depending on the equipment used for the

installation (ASTM D5092 and D6725; ASTM, 2003b and 2003c). Regardless of the method of installation, the filter pack should be sized appropriately to retain most of the formation materials.

The most common protected-screen method for installing direct push method wells is to advance an outer drive casing equipped with an expendable drive tip to the target depth. The well casing and screen are then assembled, lowered inside the drive casing, and anchored to the drive tip. The drive casing seals off the formations through which it has been advanced, protecting the well casing and screen from clogging and from passing through potentially contaminated intervals. The position and length of the screen should be selected to match the thickness of the monitoring zone, which can be determined by using additional information, such as CPT logs or continuous soil boring logs.

When direct push method wells are installed in non-cohesive, coarse-grained formations, the formation can be allowed to collapse around the screen (if this technique is not prohibited by state well installation regulations) after it is placed at the target depth since turbidity problems are unlikely. When turbidity is likely to pose a problem for groundwater sample quality, a number of methods for installing filter packs are available. The filter pack can be poured or tremied into place as the drive casing is removed. Depending on the relative size of the drive casing and well, however, it may be difficult to introduce filter pack or annular seal materials downhole unless the hole is in a cohesive formation that will remain open as the drive casing is removed. Typical inside diameters of direct push wells range from 0.5-inch (schedule 80 PVC) to 2 inches (schedule 40 PVC), and the maximum inside diameter of drive casing is 3.5 inches. The table below provides a reference for understanding the relationship between inside diameters of direct push drive casing, the outside diameter of well casing and screen, and the annular space available for filter packs.

ID Of Well Casing (in.)	OD of Well Casing (in)	Annular Space with 1.8 in OD Drive Casing (in)	Annular Space with 3.5 in OD Drive Casing (in)
0.5	0.84	0.66	2.16
0.75	1.05	0.45	1.95
1.0	1.32	0.18	1.68
1.25	1.66	NA	1.34

For the best control of filter pack placement and grain size, “sleeved” or “prepacked” well screens can be used. Pre-packed screens are generally composed of a rigid Type I PVC screen surrounded by a pre-sized filter pack. The filter pack is held in place by a stainless-steel wire mesh (for organic contaminants) or food-grade plastic mesh (for inorganic contaminants), such as polyethylene, that is anchored to the top and bottom of the screen. Sleeved screens consist of a stainless-steel wire mesh jacket filled with a pre-sized filter-pack material, which can be slipped over a PVC pipe base with slots of any size.

Annular seals and grout should be placed above the filter pack to prevent infiltration of surface runoff and to maintain the hydraulic integrity of confining or semi-confining layers, where present.

The sealing method used depends on the formation, the well installation method, and the regulatory requirements of state or local agencies. Most protected-screen installations tremie a high-solids (at least 20% solids) bentonite slurry or neat cement grout into place as the drive casing is removed from the hole. A barrier of fine sand or granular or pelletized bentonite (where water is present) may be placed above the primary filter pack before grouting to protect it from grout infiltration, which could alter the water chemistry in the screened zone. Similar to the pre-packed and sleeved screens mentioned above, modular bentonite sleeves that attach to the well screens and are advanced with the well during installation are also available. Some manufacturers provide a foam seal that expands immediately when the casing is withdrawn to form a temporary seal above the screen. A bentonite sleeve above the seal expands more slowly after the casing is withdrawn but forms a permanent seal once it hydrates. To ensure a complete seal of the annular space from the top of the annular seal to the ground surface, the grout or slurry should be placed from the bottom up. By using a high pressure grout pump and nylon tremie tube it is possible to perform bottom-up grouting in the small annular spaces of Direct Push equipment. Slurries of 20-30% bentonite or neat cement grout are most commonly used to meet state regulatory requirements. A properly constructed Direct Push installed monitoring well can provide representative water quality samples and protect groundwater resources. In addition, as with conventional wells, a properly constructed Direct Push well should have a flush-mount or above-ground well protection to prevent physical damage or tampering of the well. Small locking well plugs are also available for even 0.5-inch nominal PVC casing.

3.7 Well Completion Log:

A boring log should be completed for each boring as presented in *SOP No. 012 Geologic Logging*. A well completion log (which can be combined with the boring log) should also be completed and present, at a minimum the following:

- Well name
- Well type, i.e, piezometer, monitoring well, pumping well, etc.
- Name of individual logging the well
- Project specific information
- Well permit number
- Well survey coordinates
- 24-hour depth to water

- Completion Diagram
    - Detailed monitoring well schematic which indicates but is not limited to:
        - Borehole diameter and depth
        - Type, diameter, and depth of well
        - Type and length of casing and screen
        - Slotted screen size
        - Grain size of sand pack
        - Depth to top of screen, sand pack and bentonite seal
        - Top of the well casing in mean sea level (MSL) elevation in feet. Elevation measurements should be determined by a Professional Land Surveyor following completion of the monitoring well.
        - Top of screen, bottom of screen, and bottom of well in feet below ground surface.

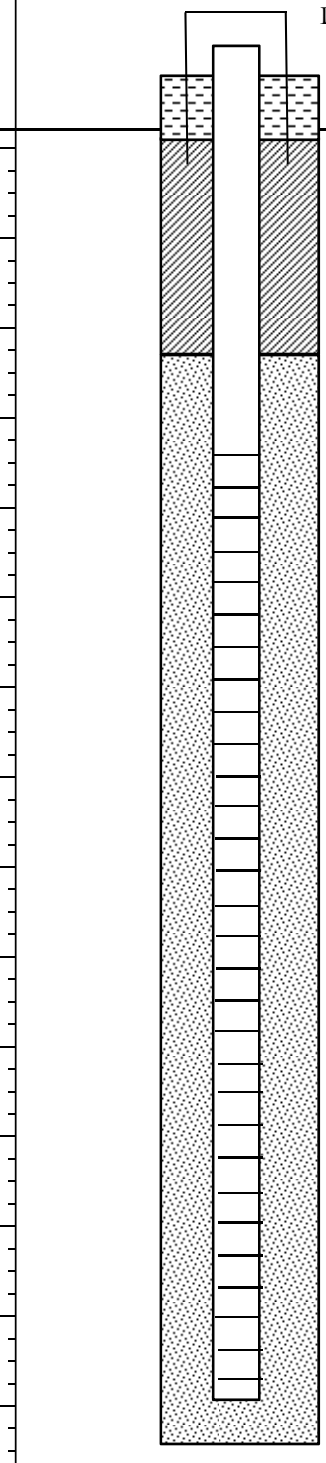
Monitoring Well Construction Log

Well ID: **Well Permit No:** Page 1 of

Project Name: Project Number: Client: Site: Borehole Location: Well Type:	Date/Time Started: Date/Time Completed: Logged by: Checked by: Driller: Development Amount (gal): Start/End - Time/Date:	Northing (ft): Easting (ft): Surface Elevation (ft), AMSL: Total Depth (ft): Depth to Water (ft): Borehole Diameter (in):

Depth (ft):

WELL CONSTRUCTION DIAGRAM



LITHOLOGIC DESCRIPTION

COMPLETION DETAILS

Well Pad

___ ft x ___ ft

Protective Cover w/Locking Lid: _____ in dia.

Outer Casing Type:

Diameter: _____ in.

Casing Amount:

_____ in. _____ lf

Casing Stickup (AGS): _____ in.

Top of Casing Elev., ft (AMSL)

_____

Riser Type:

Riser Diameter: _____ in.

Riser Amount:

_____ in. _____ lf

Riser stickup (AGS): _____ in.

Top of Riser Elev., ft (AMSL):

_____

Screen Type:

Screen Diameter: _____ in.

Screen Amount:

_____ in. _____ lf

Slot Size:

Grout Quantity:

top: bottom:

Grout Type:

Bentonite Seal

top: bottom:

Filter Pack:

top: bottom:

Grain size:

SOP No. 015
TEST PITTING
STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

The purpose of this Standard Operating Procedure (SOP) is to describe procedures for the collection of representative surface soil or sub-surface samples **from test pits**. Sampling depths are assumed to be those that can be reached without the use of a drill rig, direct-push technology, or other mechanized equipment (except for a back-hoe). Test pitting may be used for delineation of contamination and/or waste material that can be identified using field identification methods, investigation of subsurface anomalies identified by remote sensing technologies, or collection of soil samples for laboratory analysis to determine concentrations of contaminants.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with a final report.

1.1 References

SOP 005 Investigation-Derived Wastes Management
SOP 008-Surface Soil Sampling

2 EQUIPMENT

- Bound field logbook
- Sample tags
- Appropriate sample containers and labels
- Insulated cooler and ice
- Decontamination equipment and supplies
- Personal protective clothing and equipment as required by the site-specific HASP
- Stainless steel or aluminum trays or bowls
- Stainless steel shovels, trowels, spoons, or spatulas
- Backhoe Equipment

3 PROCEDURES

Reference SOP No. 008, Surface Soil Sampling, for details concerning surface soil sampling.

3.1 General Procedures-Test Pitting

A backhoe can be used to remove sections of soil when a detailed examination of stratigraphy and soil characteristics is required. The following procedures are used for collecting soil samples from test pits or trenches:

1. Prior to any excavation with a backhoe, it is imperative to ensure that all sampling locations are clear of overhead and buried utilities.

2. Review the site specific HASP and ensure that all safety precautions including appropriate monitoring equipment are installed as required.

3. Using the backhoe, excavate a trench at least three feet wide.to the specified depth. Place excavated soils on plastic sheets. Excavated material must be managed in accordance with SOP 005 INVESTIGATION-DERIVED WASTES MANAGEMENT.

4. Do not enter an unprotected trench! Trenches greater than five feet deep must be sloped or protected by a shoring system, as required by Occupational Safety and Health Administration (OSHA) regulations. OSHA standards require that trenches greater than 5 feet deep be inspected daily and as conditions change by a competent person prior to worker entry to ensure elimination of excavation hazards. A competent person is an individual who is capable of identifying existing and predictable hazards or working conditions that are hazardous, unsanitary, or dangerous to employees and who is authorized to take prompt corrective measures to eliminate or control these hazards and conditions.

5. A shovel is used to remove a one to two inch layer of soil from the vertical face of the pit where sampling is to be done.

6. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Coring devices are preferred due to the instability of pit faces. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In cases where sampling points cannot be reached from the surface and entry into the pit may be unsafe, samples can be collected directly from the backhoe bucket.

7. If VOC analyses are required, consideration must be given to the procedure used to collect the volatile organic compound sample. If the soil being sampled is cohesive and holds its in situ texture in the spoon, the syringe used to collect the sub-sample for Method 5035A should be plugged directly from the spoon. If, however, the soil is not cohesive and crumbles when

removed from the ground surface for sampling, consideration should be given to plugging the sample for Method 5035A directly from the sample location.

8. Abandon the pit or excavation according to applicable state regulations.

3.2 Additional Backhoe Sampling Information

- Samples collected to a depth of 5 feet (ft) will be collected from the side walls and floor of the trench/test pit, as long as the side wall can be safely accessed at that depth. In some instances, safely reaching the sidewall at 5 ft bgs may not be possible and the bucket of the backhoe will be used to access soil material. If samples are being collected to represent soil concentrations at a specified depth, then the sample should consist of a composite sample from equally-spaced locations on the pit side walls (or, if present, from areas of apparent contamination based on field indicators) at the specified depth. If samples are being collected to define soil concentrations in the material surrounding the test pit (such as for confirmation of removal of contaminated material), then a separate composite sample should be collected from three equally-spaced locations (or, if present, from areas of apparent contamination based on field indicators) from each wall and the pit floor.

- Samples collected deeper than 5 ft bgs will be collected directly from the backhoe bucket using soil material contained in the bucket that is not in contact with the bucket walls. If collected from the backhoe bucket, the sample should be a composite from three equally-spaced locations within the bucket.

3.3 Field Log Information

At a minimum, field logs for test pit excavation will include the following documentation:

- Plan and profile sketches of the test pit showing materials encountered, the depth of material, and sample locations
- Sketch of the test pit and distance and direction from permanent, identifiable location marks as appropriate
- Photographs of the test pit
- GPS coordinates for the test pit
- A description of the material removed from the excavation
- A record of samples collected
- The presence or absence of water in the test pit and the depth encountered
- Other readings, or measurements taken during excavation, including field screening reading

Unless otherwise specified and the site-specific Health and Safety Plan discusses appropriate procedures, no personnel will enter the test pit. In addition, all test pits will be backfilled on the day of excavation. In most cases, excavation materials will be used to fill the test pit. In the event that highly contaminated soil is excavated and it is expected that it will be more cost-effective to remove the soil from the site rather than use it as back fill, excavated soils may be stockpiled on polypropylene and the excavation will be filled with clean soil.

4 REFERENCES

Kasper, K. *STANDARD OPERATING PROCEDURE FOR TEST PIT SAMPLING AT THE WEST KINGSTON TOWN DUMP/ URI DISPOSAL AREA SITE*. Rep: Woodard and Curran, 2002.

Sobol, J. *Backhoe Trenching/Test Pits for Sample Collection*. Rep. Boston: CDM Smith, 2012.

SERAS. *Standard Operating Procedures*. Rep: Scientific Engineering Response and Analytical Services, 2001.

SOP No. 016
EQUIPMENT DECONTAMINATION
STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) presents general guidelines and step-by-step methods for on-site decontamination of sampling equipment, heavy equipment, and personal protective equipment. Decontamination is performed as a quality assurance measure and a safety precaution. Decontamination prevents cross-contamination between samples, minimizes contaminant transport, and also helps to maintain a clean working environment for the safety of the field personnel.

Although this SOP defines on-site decontamination procedures, it is highly recommended that (1) dedicated disposable sampling implements are used whenever possible, and (2) sufficient dedicated sampling implements are taken to the field so that the need for field decontamination is eliminated or reduced. For example, in collecting groundwater samples, dedicated, disposable bailers should be used, where practicable.

Decontamination is mainly achieved by washing and rinsing with liquids which include; soap and/or detergent solutions, tap water, distilled water, hexane, and nitric acid. The actual procedure will vary depending on project-specific requirements as listed in the project-specific work plan, the type of equipment to be used, and the analytical parameters of interest.

Each task work plan will include a brief list of the decontamination procedures described in this SOP that will be required and will provide a figure showing all proposed equipment decontamination areas to be used for that task.

1.1 Referenced SOPs

SOP 005 - Management of Investigation-Derived Wastes

2 EQUIPMENT

This section contains a general list of materials that may be required to conduct field decontamination of sampling equipment. A particular project may have slightly different requirements; the -project-specific work plan should be consulted prior to gathering and shipping equipment to the site.

- Concrete or lined decontamination pad (as required by project planning documents)

- Plastic sheeting
- Garden-type water sprayers
- Pressure washer, if required
- Portable steam cleaner, if required
- Cleaning brushes
- Distilled water
- Phosphate-free detergent (e.g., Liquinox® or Alconox®)
- Potable water supply
- Hexane (pesticide grade)
- 10% Nitric acid
- Chemical-free paper towels or shop cloths
- Cleaning brushes and scrapers
- Aluminum foil
- Drop cloth or plastic sheeting
- Gloves; safety glasses, protective clothing
- Cleaning containers (e.g., buckets, basins, pans)
- Chemically-compatible dedicated squirt or spray bottles for each solvent above and/or distilled water

Additional supplies such as those listed below could be required for waste disposal:

- Trash bags
- Trash containers
- 55-Gallon drums
- Metal or plastic buckets with lids for storage and disposal of decontamination liquids

3 METHODOLOGIES

Where feasible, all sampling equipment should be cleaned prior to use and dedicated to one sampling location for each sampling event to minimize the need for cleaning equipment in the field. In some instances, the use of dedicated sampling equipment may not be a practical option, depending on the scope of the project.

In general, decontamination is accomplished by manually scrubbing, washing, or spraying equipment with one or more of the following: detergent solutions, tap water, distilled water, steam, acids, or solvents. Equipment can be allowed to air dry after being decontaminated or may be wiped dry with chemical-free paper towels, if immediate use is necessary.

A decontamination area should be set up before any personnel or equipment enters areas of potential exposure. The contaminants encountered and type of equipment used will dictate the type of field decontamination procedures required.

At a minimum, the following procedures will be used for decontamination of sampling equipment that comes in direct contact with the sample:

1. Remove adhered material from the sampling equipment by brushing and/or rinsing with tap water.
2. Wash with non-phosphate detergent and tap water.
3. Rinse with distilled water.
4. Repeat the first three steps as necessary until all residue is removed.
5. If metals are a constituent of interest, rinse with 10% nitric acid.
6. Rinse with distilled water.
7. If organics are constituents of interest, rinse with pesticide-grade hexane and allow to air dry on a clean surface.
8. Rinse with distilled water.
9. Air dry or dry with clean, chemical free paper towels or shop cloths.

If metals are not a constituent of interest for sample analysis, the nitric acid rinse and the subsequent distilled water rinse steps can be eliminated. If organics are not a constituent of interest for sample analysis, the hexane rinse and the subsequent distilled water rinse steps can be eliminated.

3.1 Decontamination Area

During the project planning activities, a localized decontamination area was established and is provided on **Figure 1** (attached). The location of the decontamination area will be such that fluids and solids wastes can be managed in a controlled area with minimal risk to the surrounding environment. Should adverse weather conditions occur, the decontamination area may be moved indoors to the alternate location provided on **Figure 1**.

Smaller decontamination tasks, such as the cleaning of soil or water sampling equipment, and Geoprobe drive rods and Macro-Core barrels, may take place at the sampling location. In this case, all required decontamination supplies and equipment must be brought to the sampling location. This decontamination will use various containment systems to capture the decontamination IDW, which can then be transferred to larger containers as needed and transported to the IDW storage facility.

3.1.1 Large Equipment Decontamination Area

In some cases, for heavy equipment such as earthmoving equipment, an existing concrete pad can be used for decontamination activities. In other cases, one may need to be constructed. This determination will be made prior to the use of heavy equipment for earthmoving. The concrete pad, shall be lined with heavy-gauge plastic sheeting and include a collection system to capture decontamination Investigation Derived Waste (IDW). The decontamination fluids may then be transferred to 55-gallon drums (with lids) or 5-gallon buckets with tight fitting lids and transported to the IDW storage facility.

3.1.2 Drilling Equipment Decontamination Area

Decontamination of downhole drilling equipment (drill bits, hollow-stem augers, and drilling rods) shall be completed using a decontamination pad; which will be constructed in the decontamination area (**Figure 1**). The decontamination pad should be constructed in an area known or believed to be free of contamination; in a manner that prevents leakage; constructed on level ground; and lined with heavy plastic sheeting.

3.2 Health and Safety Precaution

Decontamination procedures may involve:

- Potential exposure to constituents within the medium being investigated or solvents employed
- Physical hazards associated with the operation of the decontamination equipment

When decontamination is performed on equipment which has been in contact with the constituents of interest or when the quality assurance objectives of the project require decontamination with chemical solvents, the measures necessary to protect personnel should be addressed in the Health and Safety Plan. The Health and Safety Plan must be approved by the project Health and Safety Officer before work commences, must be distributed to all personnel performing equipment decontamination and must be adhered to as field activities are performed. Material Safety Data Sheets for any solvents stored or used on-Site should be should be available at the Site.

At a minimum, eye protection, safety shoes, and gloves are to be worn. There are several types of gloves that may be worn, depending on equipment being cleaned, type and extent of equipment contamination, and cleaning solutions or solvents being used.

Polyvinyl gloves may be worn when the equipment to be decontaminated is not heavily coated with constituents such as tars/oils. In cases where heavy accumulations of tars/oils are present on the equipment, neoprene or similar chemically compatible gloves are recommended. If a potential for skin contact exists, protective clothing should be worn.

3.3 General Equipment Decontamination Procedures

All sampling equipment must be decontaminated before use to ensure that contaminants have not been introduced to the sample during the sampling process through contact with the sampling device. Monitoring well riser pipes, screens and drilling augers must also be decontaminated, as appropriate, to prevent the introduction of constituents.

Unless the decontaminated sampling devices that will come in contact with samples are to be used immediately, they should be wrapped in aluminum foil, shiny side out, and stored in a designated "clean" area. Field equipment can also be stored in plastic bags to eliminate the potential for

contamination. Larger size equipment, such drill rods, augers, backhoe buckets, etc. need not be wrapped or covered. This equipment should be stored on horses or otherwise, kept from storage directly on the ground surface. Field equipment should be inspected and decontaminated prior to use if the equipment has been stored for long periods of time.

3.4 Personnel and Personal Protective Equipment (PPE)

Decontamination of personnel and PPE prevents undesired human-health exposure to contaminants via ingestion, absorption, and inhalation.. Any further concerns regarding personnel and PPE decontamination procedures may be addressed directly with the Health and Safety Officer and/or Project Manager.

3.5 Decontamination of Sampling Equipment

Conduct consistent decontamination of sampling equipment to ensure the quality of the samples collected. Decontaminate all sampling equipment that comes into contact with potentially contaminated samples. Disposable equipment intended for one-time use that is factory-wrapped generally does not need to be decontaminated before use, unless evidence of contamination is present.

Disposable equipment, such as disposable bailers, spoons, TerraCore® or Encore® VOC samplers, is preferred over reusable equipment; use wherever appropriate. Decontaminate sampling equipment, including split-spoon samplers, Geoprobe Macro-Core cutting shoes, hand augers, reusable bailers, spoons, trowels, and shovels used to collect samples for chemical analyses before sampling at a new sampling location. All decontamination fluids will be captured in a containment system as appropriate. The decontamination fluids may then be transferred to 55-gallon drums (with lids) or 5-gallon buckets with tight fitting lids and transported to the IDW storage facility.

Take the following steps to decontaminate non-dedicated, non-disposable sampling equipment:

1. Remove as much gross contamination (such as pieces of soil) as possible off equipment at the sampling site.
2. Wash water-resistant equipment thoroughly and vigorously with potable water containing non-phosphate laboratory-grade detergent such as Liquinox®, Alconox®, or equivalent, and using a bristle brush or similar utensil to remove any remaining residual contamination.
3. Rinse equipment thoroughly with potable water.
4. Rinse equipment thoroughly with distilled water.
5. Repeat the first three steps as necessary until all residue is removed.
6. Rinse with 10% nitric acid, if metals are a constituent of interest.
7. Rinse with distilled water.
8. If organics are constituents of interest, rinse with pesticide-grade hexane and allow to air dry on a clean surface.
9. Rinse with distilled water.

10. Air dry at a location where dust or other fugitive contaminants may not contact the sample equipment. Alternatively, wet equipment maybe dried with a clean, disposable paper towel to assist the drying process. All equipment should be dry before reuse.
11. If the equipment is not used soon after decontamination, it should be covered or wrapped in new, oil-free aluminum foil or new, unused plastic bags to protect the decontaminated equipment from fugitive contaminants before reuse.
12. Store decontaminated equipment at a secure, unexposed location out of the weather and any potential contaminant exposure.

If metals are not a constituent of interest for sample analysis, the nitric acid rinse and the subsequent distilled water rinse steps can be eliminated. If organics are not a constituent of interest for sample analysis, the hexane rinse and the subsequent distilled water rinse steps can be eliminated.

3.6 Decontamination of Groundwater Sampling Pumps

(Note: This procedure does not apply to dedicated submersible pumps which have been permanently installed in wells.)

Proper decontamination between wells is essential to avoid introduction contaminants from the sampling equipment to another well. If peristaltic pumps are being used, it is necessary only to replace the pump head tubing after sampling each well. If sampling with submersible pumps that come into direct contact with groundwater, the equipment must be decontaminated. The following procedure will be used to decontaminate submersible pumps before and between groundwater sample collection points, as well as the end of each day of use.

Field-site cleaning procedure for submersible pumps and pump tubing:

Step 1: Preparation.

a. Pre-clean standpipes (one standpipe for each cleaning solution to be used). The standpipes need to be of sufficient height to supply necessary head for proper pump operation. Separate standpipes are designated for detergent solution and tap water rinse, distilled (DIW) rinse, and blank water. Double-bag each cleaned standpipe for transport to the field site.

b. Estimate the volumes of cleaning solutions and blank water that will be needed for the decontamination process.

c. Prepare the volumes of cleaning solutions needed for the field effort, using appropriate bottles for short-term storage and transport.

Step 2: Detergent wash and tap water rinse.

a. Put on disposable, powderless gloves. Rest pump in a washbasin or pail partially filled with detergent solution and clean exterior of pump and tubing with a soft brush. Rinse thoroughly with

tap water. (DIW can be used instead of tap water, but is less efficient in detergent removal and requires a greater volume of water than tap water.)

b. Place pump into standpipe, add detergent solution to level above pump intake, and route the intake and discharge ends of pump tubing to the standpipe.

c. Begin pumping:

i. Record the pumping rate.

ii. Record the time it takes to fill the sample tubing.

iii. Calculate the time it takes for a segment of solution to complete one cycle.

d. Circulate detergent solution for about three cycles through the tubing and back to the standpipe. If possible, pump detergent solution through tubing at alternating high and low speeds, and (or) introduce air segments between aliquots of the detergent solution to increase cleaning efficiency.

e. Remove the discharge end of tubing from the standpipe and pump about two tubing volumes of detergent solution to 5-gallon bucket, adding fresh solution to the standpipe as needed. Remove pump from standpipe.

f. Rinse detergent from standpipe with tap water until sudsing stops.

g. Rinse pump exterior with tap water. Place rinsed pump into the tap water/DIW standpipe; add tap water/DIW to level above pump intake. Begin pumping through sample tubing. Do not recirculate rinse water, but add water as needed to maintain water level above pump intake. Continue for five or more tubing volumes. Direct rinse water to 5-gallon bucket, away from the vicinity of the wellhead and sampling area and (or) contain as required for disposal.

h. Collect rinse water into a small bottle and stop the pump. Shake the bottle—if sudsing is observed in the rinse water, continue the rinse procedure until no suds appear in the rinse water. Change gloves.

Step 3: Check sampling requirements.

— If a pump will be used to collect samples for inorganic-constituent analysis, go to Step 4.

—Complete Step 4 if a pump will be used to collect samples for analysis of both inorganic and organic analytes and then go to Step 5.

—If a pump will be used to collect samples for organic-compound analysis only, go to Step 5.

Step 4: DIW rinse.

A separate DIW rinse is not required if DIW was substituted for tap water.

a. Use a clean DIW-dedicated standpipe (not the tap water standpipe) and rinse the standpipe with DIW. Rinse pump exterior with DIW. Place pump into the DIW standpipe and add DIW to level above pump intake. Change gloves.

b. Start pumping DIW. Rinse DIW through sample tubing without recirculating, using about three tubing volumes of DIW. Keep the DIW level above pump intake.

c. If collecting field blanks to verify that the pump has been adequately cleaned:

i. Change gloves. Rinse clean blank-water standpipe with DIW. Rinse pump exterior with blank water.

ii. Place pump into the standpipe and add DIW to cover the pump intake.

iii. Turn on pump and displace any water residing in the pump and tubing. Continue pumping DIW for one tubing volume before collecting the blank sample.

The decontamination fluids may then be transferred from 5-gallon buckets and/or standpipes described above to 55-gallon drums (with lids) or 5-gallon buckets with tight fitting lids and transported to the IDW storage facility.

Storage of the cleaned submersible pump and tubing:

1. Place pump into two clean, non-contaminating storage bags and tie the bags shut.

2. Cover the pump reel and tubing with doubled plastic bags or sheeting for transport to the next site.

3. On reaching the next monitoring well, place the pump in the well casing and wipe dry both the power and discharge lines with a chemical-free paper towel as the pump is lowered.

For long-term storage (longer than 3 days), the pump and exterior and interior of the tubing must be dry before being placed into plastic bags. Tubing can be dried by blowing filtered air or filtered (inert) gas through the tubing. If tubing cannot be dried, store chilled to prevent bacterial growth. If bacterial growth has occurred, re-clean before use.

3.7 Decontamination of Measurement Devices & Monitoring Equipment

For water quality instruments, oil-water interface indicators, water level indicators, continuous water level data loggers, and other field instruments that have the potential to come into contact with site media, at a minimum, wash with dilute laboratory-grade detergent (Liquinox® or similar) and double rinse with potable and distilled water before and after each use or by using a similar procedure as discussed in Section 3.5. All decontamination fluids will be captured in a containment system as appropriate. The decontamination fluids may then be transferred to 55-gallon drums (with lids) or 5-gallon buckets with tight fitting lids and transported to the IDW storage facility.

3.8 Decontamination of Subsurface Drilling Equipment

Drilling equipment and associated materials (that is, drill bits, augers, and drilling stems) will be decontaminated by the drilling contractor prior to any drilling operations and between borings. These decontamination activities shall be performed using the decontamination pad located in the decontamination area as described in Section 3.1.2 above. The decontamination shall be performed using the following basic sequence:

1. Remove as much gross contamination as possible off equipment at the sampling site.
2. Wash equipment thoroughly and vigorously with potable water using a high-pressure washer and/or steam cleaner. A bristle brush is also suggested to remove any persistent gross contamination.
3. Air dry at a location where dust or other fugitive contaminants may not contact the sample equipment. All equipment should be dry before reuse.
4. Store decontaminated equipment at a location away from any potential exposure from fugitive contamination.

The decontamination fluids will then be transferred from the decontamination pad to 55-gallon drums (with lids) or 5-gallon buckets with tight fitting lids and transported to the IDW storage facility.

All down-hole Geoprobe tools (drive rods, Macro-Core barrels, etc.) that come in direct contact with potentially contaminated soil or groundwater shall be decontaminated between each sampling location, and may take place at the sampling location using a mobile decontamination platform with a containment system to capture the decontamination IDW. The decontamination fluids may then be transferred to 55-gallon drums (with lids) or 5-gallon buckets with tight fitting lids and transported to the IDW storage facility.

Take the following steps to decontaminate the down-hole Geoprobe tools:

1. Remove as much gross contamination as possible off equipment at the sampling site.
2. Wash equipment thoroughly and vigorously with potable water using a high-pressure washer and/or steam cleaner. A bristle brush is also suggested to remove any persistent gross contamination.
3. Air dry at a location where dust or other fugitive contaminants may not contact the sample equipment. All equipment should be dry before reuse.
4. Store decontaminated equipment at a location away from any potential exposure from fugitive contamination.

3.9 Decontamination of Heavy Equipment

Wash earthwork equipment (such as excavators and back-hoes) with high-pressure potable water, if possible, before leaving a contaminated area using similar steps as outlined in Section 3.8, otherwise the equipment may be moved to the decontamination area discussed in Section 3.1.1. Hand washing with a brush and detergent, followed by a potable water rinse, can also be used. In some instances, tires and tracks of equipment maybe only need to be thoroughly brushed with a dry brush. Take particular care with the components in direct contact with contaminants, such as tires and backhoe buckets. Any part of earthwork equipment that may come in direct contact with analytical samples (that is, sampling from the excavator bucket) must be thoroughly decontaminated before excavation activities and between sample locations.

4 QUALITY ASSURANCE/QUALITY CONTROL

To ensure that sampling equipment is cleaned properly and sample cross-contamination does not occur, field rinsate blanks will be collected as required by the Sampling and Analysis Plan. A rinsate blank will consist of pouring deionized organic-free water over the specific sampling device or pouring it through the device after it has been cleaned. The rinsate sample is collected in the field under the same conditions as occurred for the sampling activity, and is handled exactly like any other samples collected that day.

Generally, one rinsate blank is collected each day of sampling or at a rate of 1 per 20 for each parameter, whichever is less, for each matrix being sampled or for each type of sampling instrument decontaminated and reused per day. The rinsate samples are analyzed for the specific parameters of concern (for each matrix). Rinsate blanks should be labeled like a routine environmental sample, and laboratory analysis instructions should be included on the chain-of-custody form.

Rinsate blanks are not required if dedicated sampling equipment is used. Additional quality assurance samples may be collected if deemed necessary by project specific requirements. All project specific quality assurance sampling are defined in the QAPP.

5 DOCUMENT AND RECORD KEEPING

The field team leader will maintain a record of the decontamination procedures. Notations shall be made in the field logbook concerning the decontamination procedures and which equipment was decontaminated.

The following information should be recorded in the Field Logbook:

- Decontamination personnel
- Decontamination solutions used
- Start and finish date and time
- Location of decontamination activities
- General methods used, tools used, and observations, including any deviations from this SOP
- Location and amount of decontamination IDW collected, stored, and/or disposed, including the sources (e.g., well or boring numbers) of the IDW (see SOP *05 – Management of Investigation-Derived Wastes*)
- Any spills or releases, and associated corrective actions taken.

6 REFERENCES

United States Environmental Protection Agency, January 1991, Compendium of ERT Groundwater Sampling Procedures: Washington, D.C., EPA 540/P-91/007.

United States Environmental Protection Agency, December 1987, A Compendium of Superfund Field Operations Methods: Washington, D.C., EPA 540/P-87/001.

ARM Group Inc.
Earth Resource Engineers and Consultants

0 50 100 200 Feet

SOP No. 16 - Equipment Decontamination Areas

September 1, 2015

EnviroAnalytics Group	Sparrows Point Terminal
ARM Project 150241M	Baltimore County, MD

Figure 1

SOP No. 017
CALIBRATION OF FIELD INSTRUMENTS
STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

The purpose of this standard operating procedure (SOP) is to provide a framework for calibrating field instruments. Water quality parameters for groundwater and surface waters include temperature, pH, dissolved oxygen, specific conductance, oxidation/reduction potential (ORP), and turbidity. This SOP supplements, but does not replace, EPA analytical methods listed in 40 CFR 136 and 40 CFR 141 for temperature, dissolved oxygen, conductivity/specific conductance, pH and turbidity. The probe readings for pH, dissolved oxygen, and specific conductance are automatically corrected for temperature.

With the exception of turbidity, the remaining water quality parameters are measured using probes included on the YSI ProPlus multimeter and Horiba Water Quality Meter U-50 Series multimeter. For groundwater monitoring, the instrument must be equipped with a flow-through-cell (Horiba Flow Through Cell U-50 Series) and the display/logger or computer display screen needs to be large enough to simultaneously contain the readouts of each probe in the instrument. Turbidity is measured using a separate instrument. It must not be measured in a flow-through-cell because the flow-through-cell acts as a sediment trap. This procedure is applicable for use with the *EPA Region I Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells.*

Other instruments requiring calibration checks or field calibration include the XRF meter, used for the detection of lead based paint, and PID meter, used for the detection of volatile organic and inorganic compounds. The calibration checks for these additional pieces of equipment are also described in this SOP.

2 HEALTH AND SAFETY WARNINGS

Read all labels on the standards and note any warnings on the labels. Wear appropriate personal protection equipment (e.g., gloves, eye shields, etc.) when handling the standards. If necessary, consult the Material Safety Data Sheets (MSDS) for additional safety information on the chemicals in the standards.

3 GENERAL

All monitoring instruments must be calibrated before they are used to measure environmental samples. For instrument probes that rely on the temperature sensor (pH, dissolved oxygen, specific conductance, and oxidation/reduction potential [ORP]), each temperature sensor needs to be checked for accuracy against a thermometer that is traceable to the National Institute of Standards and Technology (NIST). Before any instrument is calibrated or used to perform environmental measurements, the instrument must stabilize (warm-up) according to manufacturer's instructions and must have no air bubbles lodged between the probe and probe guard.

Most projects will require at least two standards to bracket the expected measurement range. This means that one standard is less than the expected value and one is higher. When an environmental sample measurement falls outside the calibration range, the instrument must be recalibrated to bracket the new range before continuing measurements. Otherwise, the measurements that are outside the calibration range will need to be qualified.

This SOP requires that the manufacturer's instruction manual (including the instrument specifications) accompany the instrument into the field.

4 FREQUENCY OF CALIBRATION

At a minimum, the instrument is calibrated prior to use on the day the measurements are to be performed. A post calibration check at the end of the day is performed to determine if the instrument drifted out of calibration. Some projects may require more frequent calibration checks throughout the day in addition to the check at the end of the day. For these checks, the instrument can be recalibrated during the day if the instrument drifted out of calibration and only the data measured prior to the check would need to be qualified. The calibration/post calibration data information is recorded in Table 1.

Instruments (e.g., sonde) that monitor continuously over a period of time are calibrated before deployment. When these instruments are recovered, the calibration is checked to determine if any of them drifted out of calibration.
Some instruments lose their calibration criteria when they are turned off. Those instruments can either be left on all day (battery dependent) or calibrated at each sampling location. If they are calibrated at each sampling location, a post calibration check is not needed.

Ideally, the temperature of the standards should be close to the temperature of the ambient water that is being measured.

5 CALIBRATION PROCEDURES

Prior to calibration, all instrument probes and cable connections must be cleaned and the battery checked according to the manufacturer's instructions. Failure to perform these steps (proper maintenance) can lead to erratic measurements.

If a multi-probe instrument is to be used, program the instrument to display the parameters to be measured (e.g., temperature, pH, percent dissolved oxygen, mg/L dissolved oxygen, specific conductance, and ORP).

The volume of the calibration solutions must be sufficient to cover both the probe and temperature sensor (see manufacturer's instructions for the volume to be used).

Check the expiration date of the standards. Do not use expired standards.

All standards are stored according to manufacturer instructions.

5.1 Temperature

SOP Reference: Current

Equipment Manual: YSI ProPlus; Horiba Water Quality Meter U-50 Series

Introduction:

Most instrument manuals state there is no calibration of the temperature sensor, but the temperature sensor must be checked to determine its accuracy. This accuracy check is performed at least once per year and the accuracy check date/information is kept with the instrument. If the accuracy check date/information is not included with the instrument or the last check was over a year, the temperature sensor accuracy needs to be checked at the beginning of the sampling event. If the instrument contains multiple temperature sensors, each sensor must be checked. This procedure is not normally performed in the field. If the instrument is obtained from a rental company, the rental company should performed the calibration check and include with the instrument documentation that it was performed.

Calibration (Verification) Procedure:

1. Fill a container with water and adjust the water temperature to below the water body's temperature to be measured. Use ice or warm water to adjust the temperature.
2. Place a thermometer that is traceable to the National Institute of Standards and Technology (NIST) and the instrument's temperature sensor into the water. Wait for both temperature readings to stabilize.
3. Compare the two measurements. The instrument's temperature sensor must agree with the reference thermometer measurement within the accuracy of the sensor (e.g., ±0.2 °C). If the measurements do not agree, the instrument may not be working properly and the manufacturer needs to be consulted.
4. Adjust the water temperature to a temperature higher than the water body to be measured.
5. Compare the two measurements. The instrument's temperature sensor must agree with the reference thermometer measurement within the accuracy of the sensor (e.g., ± 0 .2 ° C). If the measurements do not agree, the instrument may not be working properly and the manufacturer needs to be consulted.

5.2 pH (electrometric)

SOP Reference: Current

Equipment Manual: YSI ProPlus; Horiba Water Quality Meter U-50 Series

Introduction:

The pH of a sample is determined electrometrically using a glass electrode.

Choose the appropriate buffered standards that will bracket the expected values at the sampling locations. If the water body's pH is unknown, then three standards are needed for the calibration: one close to seven, one at least two pH units below seven, and the other at least two pH units above seven. Instruments that will not accept three standards will need to be re-calibrated if the water sample's pH is outside the initial calibration range described by the two standards.

Calibration Procedure:

1. Allow the buffered standards to equilibrate to the ambient temperature.
2. Fill calibration containers with the buffered standards so each standard will cover the pH probe and temperature sensor.
3. Remove probe from its storage container, rinse with deionized water, and remove excess water.
4. Select measurement mode. Immerse probe into the initial standard (e.g., pH 7).
5. Wait until the readings stabilize. If the reading does not change within 30 seconds, select calibration mode and then select "pH". Enter the buffered standard value into instrument.
6. Remove probe from the initial standard, rinse with deionized water, and remove excess water.
7. Immerse probe into the second standard (e.g., pH 4). Repeat step 5.
8. Remove probe from the second standard, rinse with deionized water, and remove excess water. If instrument only accepts two standards, the calibration is complete. Go to step · 11. Otherwise continue.
9. Immerse probe in third buffered standard (e.g., pH 10) and repeat step 5.
10. Remove probe from the third standard, rinse with deionized water, and remove excess water.
11. Select measurement mode, if not already selected. To ensure that the initial calibration standard (e.g., pH 7) has not changed, immerse the probe into the initial standard. Wait for the readings to stabilize. The reading should read the initial standard value within the manufacturer's specifications. If not, re-calibrate the instrument. If re-calibration does not help, the calibration range may be too great. Reduce calibration range by using standards that are closer together.
12. The calibration is complete. Rinse the probe with deionized water and store the probe according to manufacturer's instructions.
13. Record the calibration information on Table 1.

5.3 Dissolved Oxygen

SOP Reference: Current

Equipment Manual: YSI ProPlus; Horiba Water Quality Meter U-50 Series

Introduction:

Dissolved oxygen (DO) content in water is measured using a membrane electrode. To insure proper operation, the DO probe's membrane and electrolyte should be replaced prior to calibration for the sampling event. The new membrane may need to be conditioned before it is used; consult manufacturer's manual on how the conditioning is to be performed. Failure to perform this step may lead to erratic measurements. Before performing the calibration/measurements, inspect the membrane for air bubbles and nicks.

Note: some manufacturers require an altitude correction instead of a barometric correction. In that case, enter the altitude correction according to the manufacturer's directions in Step 5 and then proceed to Step 6.

Note: some instruments have a built-in barometer. Follow the manufacturer's instructions for entering the barometric value in step 5.

Calibration Procedure:

1. Gently dry the temperature sensor and remove any water droplets from the DO probe's sensor membrane according to manufacturer's instructions. Note that the evaporation of moisture on the temperature sensor or DO probe may influence the readings during calibration.
2. Create a 100 percent water-saturated air environment by placing a wet sponge or a wet paper towel on the bottom of the DO calibration container. Place the DO probe into the calibration container. The probe is loosely fitted into the calibration container to prevent the escape of moisture evaporating from the sponge or paper towel while maintaining ambient pressure (see manufacturer's instructions). Note that the probe and the temperature sensor must not come in contact with these wet items.
3. Allow the confined air to become saturated with water vapor (saturation occurs in approximately 10 to 15 minutes). During this time, tum on the instrument to allow the DO probe to warm-up. Select the measurement mode. Check the temperature readings. Readings must stabilize before continuing to the next step.
4. Select calibration mode; then select "DO %".
5. Enter the local barometric pressure (usually in mm of mercury) for the sampling location into the instrument. This measurement must be determined from an on-site barometer. Do not use barometric pressure obtained from the local weather services unless the pressure is corrected for the elevation of the sampling location. [Note: inches of mercury times 25.4 mm/inch equals mm of mercury or consult Oxygen Solubility at Indicated Pressure chart attached to the SOP for conversion at selected pressures].
6. The instrument should indicate that the calibration is in progress. After calibration, the instrument should display percent saturated DO.

Continued on next page…

7. Select measurement mode and set the display to read DO mg/L and temperature. Compare the DO mg/L reading to the Oxygen Solubility at Indicated Pressure chart attached to the SOP. The numbers should agree. If they do not agree within the accuracy of the instrument (usually ± 0.2 mg/L), repeat calibration. If this does not work, change the membrane and electrolyte solution.
8. Remove the probe from the container and place it into a 0.0 mg/L DO solution (see footnote). Check temperature readings. They must stabilize before continuing.
9. Wait until the "mg/L DO" readings have stabilized. The instrument should read less than 0.5 mg/L (assuming an accuracy of ± 0.2 mg/L). If the instrument reads above 0.5 mg/L or reads negative, it will be necessary to clean the probe, and change the membrane and electrolyte solution. If this does not work, try a new 0.0 mg/L DO solution. If these changes do not work, contact the manufacturer. Note: some projects and instruments may have different accuracy requirements. The 0.5 mg/L value may need to be adjusted based on the accuracy requirements of the project or instrument.
10. After the calibration has been completed, rinse the probe with tap or deionized water and store the probe according to manufacturer's instructions. It is important that all of the 0.0 mg/L DO solution be rinsed off the probe so as not to effect the measurement of environmental samples.
11. Record calibration information on Table 1.

Note: You can either purchase the 0.0 mg/L DO solution from a vendor or prepare the solution yourself. To prepare a 0.0 mg/L DO solution, follow the procedure stated in Standard Methods (Method 4500-0 G). The method basically states to add excess sodium sulfite (until no more dissolves) and a trace amount of cobalt chloride (read warning on the label before use) to water. This solution is prepared prior to the sampling event. Note: this solution can be made without cobalt chloride, but the probe will take longer to respond to the low DO concentration.

5.4 Specific Conductance

SOP Reference: Current

Equipment Manual: YSI ProPlus; Horiba Water Quality Meter U-50 Series

Introduction:

Conductivity is used to measure the ability of an aqueous solution to carry an electrical current. Specific conductance is the conductivity value corrected to 25 °C.

Most instruments are calibrated against a single standard which is near the specific conductance of the environmental samples. The standard can be either below or above the specific conductance of the environmental samples. A second standard is used to check the linearity of the instrument in the range of measurements.

When performing specific conductance measurement on groundwater or surface water and the measurement is outside the initial calibration range defined by the two standards, the instrument will need to be re-calibrated using the appropriate standards.

Calibration Procedure:

1. Allow the calibration standards to equilibrate to the ambient temperature.
2. Fill calibration containers with the standards so each standard will cover the probe and temperature sensor. Remove probe from its storage container, rinse the probe with deionized water or a small amount of the standard (discard the rinsate), and place the probe into the standard.
3. Select measurement mode. Wait until the probe temperature has stabilized.
4. Select calibration mode, then specific conductance. Enter the specific conductance standard value. Make sure that the units on the standard are the same as the instrument units. If not, convert the units on the standard to the instrument units.
5. Select measurement mode. The reading should remain within manufacturer's specifications. If it does not, re-calibrate. If readings continue to change after recalibration, consult manufacturer or replace calibration solution.
6. Remove probe from the standard, rinse the probe with deionized water or a small amount of the second standard (discard the rinsate), and place the probe into the second standard. The second standard will serve to verify the linearity of the instrument. Read the specific conductance value from the instrument and compare the value to the specific conductance on the standard. The two values should agree within the instrument specifications. If they do not agree, re-calibrate. If readings do not compare, then the second standard may be outside the linear range of the instrument. Use a standard that is closer to the first standard and repeat. If values still do not compare, try cleaning the probe or consult the manufacturer.
7. After the calibration has been completed, rinse the probe with deionized water and store the probe according to manufacturer's instructions.
8. Record the calibration information on Table 1.

Note: for projects where specific conductance is not a critical measurement it may be possible to calibrate with one standard in the range of the expected measurement.

5.5 Oxidation / Reduction Potential (ORP)

SOP Reference: Current

Equipment Manual: YSI ProPlus; Horiba Water Quality Meter U-50 Series

Introduction:

The oxidation/reduction potential is the electrometric difference measured in a solution between an inert indicator electrode and a suitable reference electrode. The electrometric difference is measured in millivolts and is temperature dependent.

Calibration Procedure:

1. Allow the calibration standard (a Zobell solution: read the warning on the label before use) to equilibrate to ambient temperature.
2. Remove the probe from its storage container and place it into the standard.
3. Select measurement mode.
4. Wait for the probe temperature to stabilize, and then read the temperature.
5. If the instrument is to be calibrated, do Steps 6 and 7. If the instrument calibration is to be verified, then go to Step 8.
6. Look up the millivolt (mv) value at this temperature from the millivolt versus temperature correction table usually found on the standard bottle or on the standard instruction sheet. You may need to interpolate millivolt value between temperatures. Select "calibration mode", then "ORP". Enter the temperature-corrected ORP value into the instrument.
7. Select measurement mode. The readings should remain unchanged within manufacturer's specifications. If they change, re-calibrate. If readings continue to change after re-calibration, try a new Zobell solution or consult manufacturer. Go to Step 9.
8. If the instrument instruction manual states that the instrument is factory calibrated, then verify the factory calibration against the Zobell solution. If they do not agree within the specifications of the instrument, try a new Zobell solution. If it does not agree, the instrument will need to be re-calibrated by the manufacturer.
9. After the calibration has been completed, rinse the probe with deionized water and store the probe according to manufacturer's instructions.
10. Record the calibration information on Table 1.

5.6 Turbidity

SOP Reference: 027

Equipment Manual: LaMotte 2020 we-wi Turbidimeter; LaMotte Turbidity Kit
Hach 2100 and 2100Qis Turbidity Meter

Introduction:

The turbidity method is based upon a comparison of intensity of light scattered by a sample under defined conditions with the intensity of light scattered by a standard reference suspension. A turbidimeter is a nephelometer with a visible light source for illuminating the sample and one or more photo-electric detectors placed ninety degrees to the path of the light source. Note: the below calibration procedure is for a turbidimeter which the sample is placed into a cuvette.

Some instruments will only accept one standard. For those instruments, the second, third, etc., standards will serve as check points.

Calibration Procedure:

1. Allow the calibration standards to equilibrate at the ambient temperature. The use of commercially available polymer primary standards (AMCO-AEPA-1) is preferred; however, the standards can be prepared using Formazin (read the warning on the label before use) according to the EPA analytical Method 180.1. Other standards may be used if they can be shown that they are equivalent to the previously mentioned standards.
2. If the standard cuvette is not sealed, rinse a cuvette with deionized water. Shake the cuvette to remove as much water as possible. Do not wipe dry the inside of the cuvette because lint from the wipe may remain in the cuvette. Add the standard to the cuvette.
3. Before performing the calibration procedure, make sure the cuvettes are not scratched and the outside surfaces are dry and free from fingerprints and dust. If the cuvette is scratched or dirty, discard or clean the cuvette respectively. Note: some manufacturers require the cuvette to be orientated in the instrument in a particular direction for accurate reading.
4. Select a low value standard such as a zero or 0.02 NTU and calibrate according to manufacturer's instructions. Note: a zero standard (approximately 0 NTU) can be prepared by passing distilled water through a 0.45 micron pore size membrane filter.
5. Select a high standard and calibrate according to manufacturer's instructions or verify the calibration if instrument will not accept a second standard. In verifying, the instrument should read the standard value to within the specifications of the instrument. If the instrument has range of scales, check each range that will be used during the sampling event with a standard that falls within that range.
6. Record calibration information on the Turbidity Calibration Log in SOP No. 027.

5.7 XRF Meter

SOP Reference: 023

Equipment Manual: INNOV-X Systems XRF Meter

Introduction:

A handheld X-Ray Fluorescence (XRF) detector can be used to conduct lead-based paint inspections on various combinations of paints and underlying substrates. The XRF detector emits high-energy X-rays which bombard a sample, causing it to fluoresce and emit secondary X-rays which are detected. Secondary X-rays are characteristic of each specific element, allowing for quantification of the materials in the sample. XRF instruments operate at a high speed and low cost per sample, and measure the sample without destructive sampling or paint removal.

The instrument is calibrated in the factory, but an accuracy check is necessary to determine if the equipment is operating properly prior to the data collection. A calibration check should be performed before the start of each testing period

Calibration (Verification)Procedure:

1. Remove the XRF from its casing and turn it on.
2. Take at least three calibration check readings of the provided paint chips with known lead concentrations. Make sure the XRF shutter lies flat against the test chip. Do not hold the chip while testing, or else the operator will be exposed to X-ray radiation. Typical paint chips for verification checks include a 0.0 mg/cm^2 negative control and a 1.02 mg/cm^2 reference material.
3. If the average (rounded to 1 decimal place) of the readings is outside of the calibration check range for the given paint chips, follow the manufacturers guidelines to correct the instrument.
4. Calibration rechecks should be completed every 4 hours or when testing is completed for the day, whichever is more frequent.

5.8 PID Meter

SOP Reference: 026

Equipment Manual: MiniRAE 3000 PID Meter

Introduction:

The PID is a portable, nonspecific, vapor/gas detector employing the principle of photoionization to detect a variety of chemical compounds, both organic and inorganic, in air. A PID is similar to a flame ionization detector (FID) in application; however, the PID can detect certain inorganic vapors but is unable to respond to certain low molecular weight hydrocarbons (such as methane and ethane).

The PID employs the principle of photoionization. The analyzer will respond to most vapors that have an ionization potential less than or equal to that supplied by the ionization source, which is an ultraviolet (UV) lamp. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and form a positive ion. Ions formed by the adsorption of photons are driven to the collector electrode. The current produced is then measured and the corresponding concentration displayed.

Calibration Procedure:

1. Press and hold [MODE] and [N/-] until you see the Password screen.
2. In Basic User Level, you do not need a password to perform calibrations. Instead of inputting a password, enter calibration by pressing [MODE]. If you inadvertently press [Y/+] and change any of the numbers, simply press [MODE] and you will be directed to the calibration menu. Zero calibration should be highlighted ([N/-] will toggle the calibration type).
3. Turn on the Zero calibration "fresh air" gas, which may be a include a gas from a cylinder, Tedlar bag, or clean ambient air
4. Press [Y/+] to start calibration. No action is required during the calibration. When Zero calibration is complete the instrument will then show the Calibration menu on its display, with Span highlighted.
5. To complete the span calibration, a cylinder of standard reference gas fitted with a 500 cc/min. flow-limiting regulator or a flow-matching regulator is the simplest way to perform this procedure. Alternatively, the span gas can first be filled into a Tedlar bag or delivered from a demand-flow regulator. Another option is to use a regulator with >500 cc/min flow but allow the excess to escape through a T or open tube.
6. You will see the name of your Span gas (the default is isobutylene) and the span value in parts per million (ppm).
7. Turn on your span calibration gas.
8. Press [Y/+] to initiate calibration. There is a 30-second countdown and the instrument performs the Span calibration automatically. It requires no actions on the part of the operator. The instrument automatically exits Span calibration and shows the Zero calibration menu. Press [MODE], which corresponds with "Back" to exit.

6 POST CALIBRATION CHECK

After the initial calibration is performed, the instrument's calibration may drift during the measurement period. As a result, you need to determine the amount of drift that occurred after collecting the measurements. The difference in value is then compared to the drift criteria or post calibration criteria described in the quality assurance project plan or the sampling and analysis plan for the project. If the check value is outside the criteria, then the measurement data will need to be qualified.

For parameters measured by the multiprobe, this is performed by placing the instrument in measurement mode (not calibration mode) and placing the probe in one or more of the standards used during the initial calibration. Wait for the instrument to stabilize and record the measurement (Table 1). Compare the new measurement value to the initial calibration value. For turbidity, place the standard in a cuvette and then into the turbidimeter, and record a measurement. For the dissolved oxygen calibration check, follow the calibration instructions steps one through three while the instrument is in measurement mode. Record dissolved oxygen value (mg/L), temperature, and barometric pressure. Compare the measurement value to the Oxygen Solubility at Indicated Pressure chart attached to this SOP. For the XRF, the post calibration check is the same as the initial check using the provided standard paint chips. For the PID meter, the span gas can be measured with the instrument in measurement mode.

The drift value should be within the criteria specified for the project, and if the drift value is outside the established criteria the data will need to be qualified. The drift criteria or the post-calibration criteria are shown below.

Measurement	Post Calibration Criteria
Dissolved Oxygen	± 0.5 mg/L of sat. value*
Specific Conductance	< 0.5 mg/L for the 0 mg/L solution, but not a negative value
pH	±5% of standard or ± 10µS/cm whichever is greater
Turbidity	± 5% of standard
ORP	±10 mv*
XRF	Average of 3 measurements within the provided calibration check range
PID	±10% of standard

Note: * Table 8.1, USEPA Region 1 *YSI 6-Series Sondes and Data Logger SOP*, January 30, 2007, revision 9.

7 DATA MANAGEMENT AND RECORD MANAGEMENT

All calibration records must be documented in the project's log book. At a minimum, include the instrument manufacturer, model number, instrument identification number (when more than one instrument of the same model is used), the standards used to calibrate the instruments (including source), the calibration date, the instrument readings, the post calibration check, and the name of the person(s) who performed the calibration. An example of a calibration log sheet is shown in Table 1.

8 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998.

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

Turbidity - Methods for the Determination of Inorganic Substances in Environmental Samples,

EP A/600/R-93/100, August 1993.

USEPA Region 1YSI6-Series Sondes and Data Logger SOP, January 30, 2007, revision 9:

USGS Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting, Techniques and Methods 1-D3.

TABLE 1
MULTIPARAMETER CALIBRATION LOG

Project Name_____ Date_____
Weather_____

Calibrated by_____ Instrument_____
Serial Number_____

Parameters	Morning Calibration	Morning Temperature	End of Day Calibration Check*	End of Day Temperature
Specific Conductance Standard #1				
Specific Conductance Standard #2				
pH (7)				
pH (4)				
pH(10)				
ORP Zobel Solution				
Dissolved Oxygen 100% water saturated air mg/L				
Dissolved Oxygen Zero Dissolved Oxygen Solution mg/L				
Barometric Pressure mm Hg		NA		NA
Turbidity Standard #1				
Turbidity Standard #2				
Turbidity Standard #3				

* For each Parameter, chose one standard as your check standard. If possible, choose the one that is closest to the ambient measurement value.

Oxygen Solubility at Indicated Pressure

Temp.	Pressure (Hg)							
	760	755	750	745	740	735	730	mm
°C	29.92	29.72	29.53	29.33	29.13	28.94	28.74	in
0	14.57	14.47	14.38	14.28	14.18	14.09	13.99	mg/l
1	14.17	14.08	13.98	13.89	13.79	13.7	13.61	
2	13.79	13.7	13.61	13.52	13.42	13.33	13.24	
3	13.43	13.34	13.25	13.16	13.07	12.98	12.9	
4	13.08	12.99	12.91	12.82	12.73	12.65	12.56	
5	12.74	12.66	12.57	12.49	12.4	12.32	12.23	
6	12.42	12.34	12.26	12.17	12.09	12.01	11.93	
7	12.11	12.03	11.95	11.87	11.79	11.71	11.63	
8	11.81	11.73	11.65	11.57	11.5	11.42	11.34	
9	11.53	11.45	11.38	11.3	11.22	11.15	11.07	
10	11.28	11.19	11.11	11.04	10.96	10.89	10.81	
11	10.99	10.92	10.84	10.77	10.7	10.62	10.55	
12	10.74	10.67	10.6	10.53	10.45	10.38	10.31	
13	10.5	10.43	10.36	10.29	10.22	10.15	10.08	
14	10.27	10.2	10.13	10.06	10	9.93	9.86	
15	10.05	9.98	9.92	9.85	9.78	9.71	9.65	
16	9.83	9.76	9.7	9.63	9.57	9.5	9.43	
17	9.63	9.57	9.5	9.44	9.37	9.31	9.24	
18	9.43	9.37	9.3	9.24	9.18	9.11	9.05	
19	9.24	9.18	9.12	9.05	8.99	8.93	8.87	
20	9.06	9	8.94	8.88	8.82	8.75	8.69	
21	8.88	8.82	8.76	8.7	8.64	8.58	8.52	
22	8.71	8.65	8.59	8.53	8.47	8.42	8.36	
23	8.55	8.49	8.43	.8.38	8.32	8.26	8.2	
24	8.39	8.33	8.28	8.22	8.16	8.11	8.05	
25	8.24	8.18	8.13	8.07	8.02	7.96	7.9	
26	8.09	8.03	7.98	7.92	7.87	7.81	7.76	
27	7.95	7.9	7.84	7.79	7.73	7.68	7.62	
28	7.81	7.76	7.7	7.65	7.6	7.54	7.49	
29	7.68	7.63	7.57	7.52	7.47	7.43	7.36	
30	7.55	7.5	7.45	7.39	7.34	7.29	T24	
31	7.42	7.37	7.32	7.27	7.22	7.16	7.11	
32	7.3	7.25	7.2	7.15	7.1	7.05	7.01)	
33	7.08	7.13	7.08	7.03	6.98	6.93	6.88	
34	7.07	7.02	6.97	6.92	6.87	6.82	6.78	
35	6.95	6.9	6.85	6.8	6.76	6.71	6.65	

36	6.84	6.79	6.76	6.7	6.65	6.6	6.55
37	6.73	6.68	6.64	6.59	6.54	6.49	6.45
38	6.63	6.58	6.54	6.49	6.44	6.4	6.35
39	6.52	6.47	6.43	6.38	6.35	6.29	6.24
40	6.42	6.37	6.33	6.28	6.24	6.19	6.15
41	6.32	6.27	6.23	6.18	6.14	6.09	6.05
42	6.22	6.18	6.13	6.09	6.04	6	5.95
43	6.13	6.09	6.04	6	5.95	5.91	5.87
44	6.03	5.99	5.94	5.9	5.86	5.81	5.77
45	5.94	5.9	5.85	5.81	5.77	5.72	5.68

Source: Draft EPA Handbook of Methods for Acid Deposition Studies, Field Operations for Surface.Water Chemistry, EP A/600/4-89/020, August 1989.

Oxygen Solubility at Indicated Pressure (continued)

Temp	Pressure (Hg)								
	725	720	715	710	705	700	695	690	mm
°C	28.54	28.35	28.15	27.95	27.76	27.56	27.36	27.17	in
0	13.89	13.8	13.7	13.61	13.51	13.41	13.32	13.22	mg/l
1	13.51	13.42	13.33	13.23	13.14	13.04	12.95	12.86	
2	13.15	13.06	12.07	12.88	12.79	12.69	12.6	12.51	
3	12.81	12.72	12.63	12.54	12.45	12.36	12.27	12.18	
4	12.47	12.39	12.3	12.21	12.13	12.04	11.95	11.87	
5	12.15	12.06	11.98	11.89	11.81	11.73	11.64	11.56	
6	11.84	11.73	11.68	11.6	11.51	11.43	11.35	11.27	
7	11.55	11.47	11.39	11.31	11.22	11.14	11.06	10.98	
8	11.26	11.18	11.1	11.02	10.95	10.87	10.79	10.71	
9	10.99	10.92	10.84	10.76	10.69	10.61	10.53	10.46	
10	10.74	10.66	10.59	10.51	10.44	10.36	10.29	10.21	
11	10.48	10.4	10.33	10.28	10.18	10.11	10.04	9.96	
12	10.24	10.17	10.1	10.02	9.95	9.88	9.81	9.46	
13	10.01	9.94	9.87	9.8	9.73	9.66	9.59	9.52	
14	9.79	9.72	9.65	9.68	9.51	9.45	9.38	9.31	
15	9.58	9.51	9.44	9.58	9.31	9.24	9.18	9.11	
16	9.37	9.3	9.24	9.17	9.11	9.04	8.97	8.91	
17	9.18	9.11	9.05	8.98	8.92	8.85	8.79	8.73	
18	8.99	8.92	8.86	8.8	8.73	8.67	8.61	8.54	
19	8.81	8.74	8.68	8.62	8.56	8.49	8.43	8.37	
20	8.63	8.57	8.51	8.45	8.39	8.33	8.27	8.21	
21	8.46	8.4	8.34	8.28	8.22	8.16	8.1	8.04	

22	8.3	8.24	8.18	8.12	8.06	8	7.95	7.89
23	8.15	8.09	8.03	7.97	7.91	7.86	7.8	7.74
24	7.99	7.94	7.88	7.82	7.76	7.71	7.65	7.59
25	7.85	7.79	7.74	7.68	7.6	7.57	7.51	7.46
26	7.7	7.65	7.59	7.54	7.48	7.43	7.37	7.32
27	7.57	7.52	7.46	7.41	7.35	7.3	7.25	7.19
28	7.44	7.38	7.33	7.28	7.22	7.17	7.12	7.06
29	7.31	7.26	7.21	7.15	7.1	7.05	7	6.94
30	7.19	7.14	7.08	7.03	6.98	6.93	6.88	6.82
31	7.06	7.01	6.96	6.91	6.86	6.81	6.76	6.7
32	6.95	6.9	6.85	6.8	6.7	6.7	6.64	6.59
33	6.83	6.78	6.73	6.68	6.83	6.58	6.53	6.48
34	6.73	6.68	6.63	6.58	6.53	6.48	6.43	6.38
35	6.61	6.56	6.51	6.47	6.42	6.37	6.36	6.27
36	6.51	6.46	6.41	6.36	6.31	6.27	6.22	6.17
37	6.4	6.35	6.31	6.26	6.21	6.16	6.12	6.07
38	6.3	6.26	6.21	6.16	6.12	6.07	6.02	5.98
39	6.26	6.15	6.11	6.06	6.01	5.97	5.92	5.87
40	6.1	6.06	6.01	5.96	5.92	5.86	5.83	5.78
41	6	5.96	5.91	5.87	5.82	5.78	5.73	5.69
42	5.91	5.86	5.82	5.77	5.73	5.69	5.64	5.6
43	5.82	5.78	5.73	5.69	5.65	5.6	5.56	5.51
44	5.72	5.68	5.64	5.59	5.55	5.51	5.46	5.42
45	5.64	5.59	5.55	5.51	5.47	5.42	5.38	5.34

Source: Draft EPA Handbook of Methods for Acid Deposition Studies, Field Operations for Surface.Water Chemistry, EP A/600/4-89/020, August 1989.

SOP No. 018
WELL DEVELOPMENT
STANDARD OPERATING PROCEDURE

1 SCOPE

This Standard Operating Procedure (SOP) provides guidance for developing monitoring wells or extraction wells following installation and prior to their designated use for data acquisition (e.g., groundwater sampling, aquifer testing). Some of these procedures may also apply to well purging conducted prior to collection of water quality samples. However, development should not be confused with purging, the purpose of which is to evacuate the monitoring well of stagnant water which may not be representative of the aquifer.

Monitoring well development is necessary to ensure that complete hydraulic communication is made and maintained between the well screen and the water-bearing formation. Development is necessary after original installation of a monitoring well to:

- Restore aquifer properties near the boring that were disturbed during drilling by reducing the compaction and mixing of grain sizes that occurred during drilling
- Remove fine-grained materials from the filter pack that were introduced during drilling and well installation, which could potentially affect water quality analyses
- Improve the hydraulic characteristics of the filter pack and the hydraulic communication between the well and the screened hydrogeologic unit by removing any drilling fluids or mud that cake the sides of the borehole or that may have invaded the adjacent natural formation
- Remove all water introduced into the borehole while drilling.

Formation characteristics change during drilling and well installation, and usually include the compaction of unconsolidated particles surrounding the annulus. In fine-grained soils, this can result in a mudwall around the boring annulus, which can impede free flow of formation water into the well. Monitoring well development physically agitates the formation around the well boring by pushing and pulling water through the filter pack and surrounding formation. This repetitive process flushes fine-grained soils into the well, where they either settle within the filter pack or are removed from the well during development and purging.

Common well development methods include surging, pumping, and bailing. The most effective technique involves using both a surge block in combination with pumping or bailing, so that water moves in both directions through the filter pack and the native formation surrounding the well screen.

This well development procedure also applies to rehabilitation of monitoring wells in which siltation has occurred. After a well has been in place for some period of time, the well depth may decrease

due to accumulation of fine soil particles (siltation), and rehabilitation will be necessary to reestablish complete hydraulic communication with the aquifer.

1.1 Referenced SOPs

016 – Equipment Decontamination

019 – Depth to Groundwater and NAPL Measurements

1.2 Definitions

(Reserved)

2 REQUIRED MATERIALS

The following equipment may be required when performing well development. Not all equipment may be required, depending on the well development method used.

- Surge block on a cable or line
- Appropriate pump (centrifugal pump, submersible pump, or peristaltic pump)
- Bailers and bailer cord
- Compressed gas source and air discharge line; water discharge line
- Storage containers for the purge water
- Water level probe and/or oil-water interface probe
- Copy of the well construction diagram
- Field logbook
- Well development sheets
- Personal protective equipment as specified in the Health and Safety Plan
- Water quality monitoring instrument capable of measuring dissolved oxygen (DO), conductivity, pH, turbidity, temperature and oxidation-reduction potential (ORP)

The various specific development procedures discussed in Section 3.2 identify the different types of equipment which may be used to develop monitoring wells or extraction wells. Exact equipment needs will be specific to the monitoring well and will depend upon the diameter of the well, the depth to water, and other factors such as project objectives and intended use of the well.

3 METHODOLOGIES

Newly installed monitoring wells shall be developed no sooner than 48 hours after installation. The entire vertical screened interval should be developed using surge blocks, bailers, pumps or other equipment that frequently reverse the flow of water through the screen and prevent bridging of the formation or filter pack particles.

3.1 General Well Development Procedures

1. The depth to water in the well and the possible presence of NAPLs are measured in accordance with *SOP 019 – Depth to Groundwater and NAPL Measurements*. The total depth of the well should be measured with a weighted tape and the result compared to the original depth reported in on the well construction form and/or the field notes.
2. Remove a small quantity of water from the well using a decontaminated pump or bailer. Measure and record initial pH, temperature, conductivity, DO, ORP, and turbidity.
3. Begin well development by surging the bottom of the well and removing any sediment that has accumulated. To do this, slowly lower a decontaminated surge block into the well so that the block is approximately 6 to 12 inches from the bottom of the well or the measured sediment level. Slowly raise and lower the surge block approximately 1 to 2 feet to create a mild surging effect at the bottom of the well. This will re-suspend accumulated sediment. Do not agitate the water violently. After several surge strokes, remove the surge block and immediately begin to pump or bail the sediment-laden water. Repeat this process until accumulated sediment is removed from the bottom of the well and total well depth is as reported on the well construction diagram and/or field notes.
4. Work upwards from the bottom of the screened interval using the same alternating techniques of surging and pumping or bailing. If an air compressor is used to remove the sediment-laden water, a filter must be installed on the compressor to prevent introduction of oil into the well.
5. The minimum volume of water (*e.g.*, three casing volumes) which must be removed during development is usually specified in the project work plan. In practice, development of the well is continued until the water removed is essentially free of suspended silt and clay particles, to the extent practicable. In some aquifers, it may not be possible to remove all suspended solids regardless of the extent of development activities. The supervising hydrogeologist is ultimately responsible for the determination that the well has been sufficiently developed and that development can be terminated.
6. Field measurements (pH, DO, ORP, specific conductance, temperature, and turbidity) can be taken as a confirmation of sufficient development. Adequate development can be verified by stable readings of these field parameters.
7. Measure and record a final depth to water and a total well depth after development. Record all well development data on the Well Development form and/or in the field logbook.

3.2 Specific Well Development Procedures

The appropriate development method will be selected for each project on the basis of the specific circumstances, objectives and requirements of that project. Further, some agencies have developed comprehensive guidelines for groundwater monitoring and subsurface investigation procedures. The provisions of this SOP will be adapted to these project-specific requirements in the project work plan. The work plan will specify the well development method(s) to be used and the rationale, including trade-offs associated with the nature of the aquifer formation, analytical objectives, well use, and client or agency requirements.

Aside from agency requirements, the criteria for selecting a well development method include well diameter, total well depth, static water depth, screen length, the intended well use, and the type of geologic materials in the aquifer.

The limitations, if any, of each specific procedure, are discussed in each of the following procedure descriptions.

3.2.1 Surging

A surge block consists of a rubber (or leather) and metal plunger attached to a rod or pipe of sufficient length to reach the bottom of the well. Well drillers usually can provide surge blocks for large diameter wells (greater than 6 inches). Surge blocks for smaller diameter wells can be constructed easily of materials readily accessible in any hardware store. A recommended design is shown in Figure 1. Surging alone will not cause sufficient well development; however, surging used in conjunction with groundwater removal *via* pumping, bailing, or air-lifting effectively develops most monitoring and extractions wells.

The procedure to be followed when using the surge block is:

1. Construct a surge block using the design in Figure 1 as guidance. Specific materials will depend upon the diameter of the well to be developed. The diameter of the plunging apparatus must be sufficient to force the groundwater in the well out through the well screen, and the rods must be of sufficient length to reach the bottom of the monitoring well.
2. Insert the surge block into the well and lower it slowly to the level of static water. Start the surge action slowly and gently above the well screen using the water column to transmit the surge action to the screened interval. A slow initial surging, using plunger strokes of 3 to 5 feet, will allow material which is blocking the well screen to disengage from the screen and become suspended.
3. After a number (5 to 10) of surge strokes, remove the surge block and purge the well using a pump or bailer. The returned water should be heavily laden with suspended fine particles. As development continues, slowly increase the depth of surging to the bottom of the well screen. For wells with long screens (greater than 10 feet) surging should be undertaken along the entire screen length in short intervals (2 to 3 feet) at a time.

Continue this cycle of surging and pumping/bailing until well development is complete.

3.2.2 Pumping

Groundwater pumping is necessary to remove large quantities of sediment-laden groundwater from a well after using the surge block. In some situations, pumping is performed without surging. Since the primary purpose of well development is to remove suspended solids from a well, the pump must be capable of moving some solids without damage. The preferred type of pump is a centrifugal pump because of its ability to pump solids. However, a centrifugal pump will work only where the depth to groundwater is less than approximately 25 feet. If depth to groundwater is too great, a positive-displacement pump such as a submersible or bladder pump will be necessary.

Well development using a pump is more effective in those wells that will yield water continuously. Effective development may not be accomplished if the pump has to be shut off to allow the well to recharge.

The procedure to be followed for well development *via* pumping is:

1. Set the intake of the pump in the center of the screened interval of the monitoring well.

2. When appropriate, use the pump to fill the monitoring well to the top of the casing and allow the water level to decline to the static level, thereby forcing water back into the formation. This action will cause water to exit the well screen and reduce the bridging of materials caused by water flowing in one direction through the well screen while pumping.

3. The water used to fill the monitoring well should be the same water removed from the well during the previous pumping cycle. The sediment previously pumped from the well must be removed from the water prior to re-introduction to the well. A steel drum can be used as a sediment-settling vessel.

Continue pumping water out from the well until well development is complete.

3.2.3 Bailing

A bailer is an effective tool for development of small diameter monitoring wells where removal of only a relatively small volume of water is required for development. A bottom-filling bailer can also be used to remove sediment-laden water from wells after using the surge block.

The procedure to be followed for well development *via* bailing is:

1. Lower the bailer into the screened interval of the monitoring well.
2. Using long, slow strokes, raise and lower the bailer in the screened interval simulating the action of a surge block.
3. Periodically bail standing water from the well to remove fine particles drawn into the well.

Continue surging the well and removing water from the well until well development is complete.

3.2.4 Air-lifting

Air-lifting with compressed air can be used to both surge and purge a monitoring well. An air compressor is used to inject gas at the bottom of the water column, driving sediment-laden water to the surface. Compressed air can also be used for "jetting" - a process by which the air stream is directed at the slots in the well screen to cause turbulence (thereby disturbing fine materials in the adjacent filter pack). Compressed air is not limited to any depth range.

The hose or pipe which will be installed in the well for jetting should be equipped with a horizontal (side) discharge nozzle and one or more small holes in the bottom of the hose to enhance the lifting of sediment during jetting.

Provisions must be made for controlling the discharge from the wells. This is generally accomplished by attaching a "tee" discharge to the top of the casing and providing drums or other containers to collect the discharged water.

Although the equipment used to develop a well using this method is more difficult to handle and use, well development using compressed air for jetting the well screen is considered to be a very effective method. This method also is the most generally applicable because it is not limited by well depth, well diameter, or depth to static water.

The procedure to be followed for well development *via* air-lifting is:

1. Lower the gas line from the gas cylinder into the well, setting it near the bottom of the screened interval. Install the water discharge control equipment at the well head.
2. Set the gas flow rate to allow continuous discharge of water from the well. The discharge will contain suspended clay and silt material.
3. At intervals during gas-lifting, especially when the discharge begins to contain less suspended material, shut off the air flow and allow the water in the well to flow out through the screened interval to disturb any bridging that may have occurred. Restart the gas flow when the water level in the well has returned to the pre-development level.
4. Jetting of the screened interval also can be done during gas-lifting of water and sediment from the well. This is accomplished by using a lateral-discharge nozzle on the gas pipe or hose and slowly moving the nozzle along the length of the screened interval. Jetting should be done beginning at the bottom of the well screen and moving slowly upwards along the screened interval. To enhance gas lifting of sediment, occasionally raise the discharge nozzle into the cased portion of the well and discharge sediment-laden water.

Continue air-lifting and/or jetting until well development is complete.

4 QUALITY ASSURANCE/QUALITY CONTROL

Development of new monitoring wells or extraction wells is the responsibility of the hydrogeologist involved in the original installation of the well. The geologist may, in fact, contract with the well driller to develop new wells under the geologist's guidance and oversight. If the project involves sampling of existing monitoring wells, the hydrogeologist is also responsible for verifying the original well construction details and determining if a previously installed well requires rehabilitation.

Monitoring Well Construction Details

A copy of the original well construction diagram for the well to be developed must be obtained from the Project Manager. This form provides critical information regarding the construction of the monitoring well and must be in the possession of the well development crew so that pertinent well construction details, such as total well depth and screened interval, are known.

Equipment Decontamination

All equipment which contacts development water or is placed inside a well should either be dedicated for use on only a single monitoring well or should be decontaminated, in accordance with *SOP 016 - Equipment Decontamination*, to prevent cross-contamination between monitoring wells or recovery wells.

Successful Development Criteria

A well has been successfully developed when one or more of the following criteria are met:

- The well yields clear, sediment-free water to the extent possible
- field measurements of pH, specific conductance, temperature, and turbidity have stabilized
- aquifer response and well yield are observed to be representative of the type of lithologic formation over which the well is screened
- the well is free of sediment, the measured well depth is consistent with the well construction diagram, and that depth is maintained for some extended period of time

Development Water Management

The work plan must specify the means for managing development and purge water. At active facilities, an active water treatment facility may be available for management of development and purge water. Otherwise, the water should be containerized until analytical results are available to determine the applicable management options.

5 DOCUMENTATION AND RECORD KEEPING

If required, a Well Development Form will be completed by the geologist or hydrogeologist conducting the development. In addition, a Field Log Book should be maintained detailing any problems or unusual conditions which may have occurred during the development process.

All documentation will be retained in the project files following completion of the project. In addition to the hard copies, files will be scanned and placed in the permanent digital project files.

6 REFERENCES

American Society of Testing and Materials, 1996, ASTM Standard D5521-05: Standard Guide for Development of Ground-Water Monitoring Wells in Granular Aquifers: West Conshohocken, Pennsylvania.

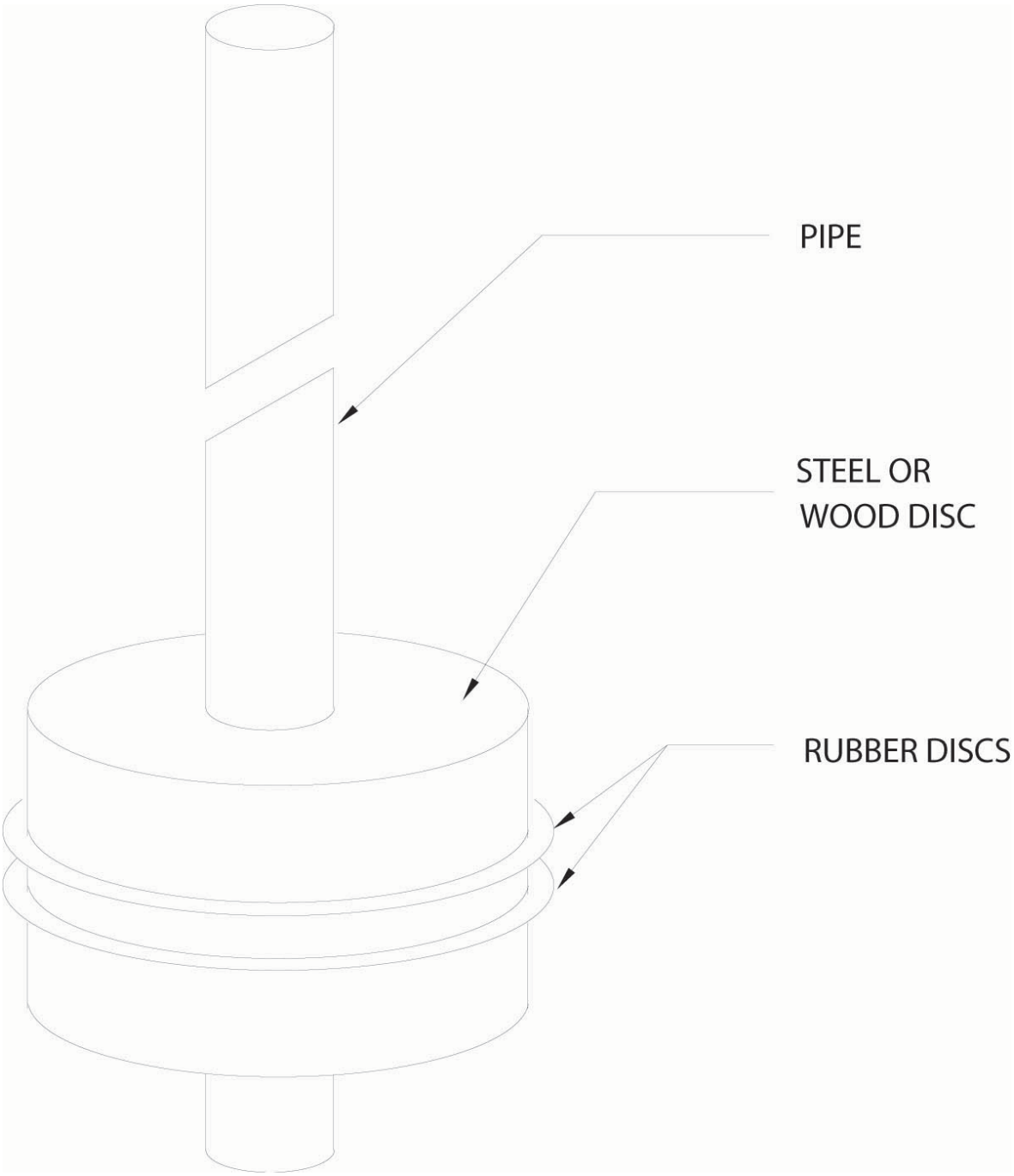


Figure 1. Example Surge Block Design

SOP No. 019
DEPTH TO GROUND WATER AND NAPL MEASUREMENTS
STANDARD OPERATING PROCEDURE

1 SCOPE

This Standard Operating Procedure (SOP) describes standard procedures to be followed for determining depth to groundwater, as well as a description of the procedures to be followed for determining the depth to and apparent thickness of any non-aqueous phase liquid (NAPL) in monitoring wells.

Generally, water level measurements from boreholes, piezometers, or monitoring wells are used to construct potentiometric surface maps and product elevation maps. These maps are used in evaluating groundwater and product migration. Potentiometric surface maps are also used to assess potential seasonal variations in groundwater movement when measurements can be made over several sampling intervals.

In order to ensure an accurate representation of groundwater and product elevations, ideally all measurements will be collected within a 24-hour period. The site-specific planning documents (Work Plan, Sampling and Analysis Plan, Scope of Work or other similar planning documents) shall be consulted to identify the specific wells to be investigated and the types and frequency of required measurements.

1.1 Referenced SOPs

SOP 010 – Field Logbook
SOP 016 – Equipment Decontamination
SOP 026 – Photoionization Detector

1.2 Definitions

(Reserved)

2 REQUIRED MATERIALS

The following list identifies the preferred types of materials to be used when measuring depth to water, depth to light NAPL (LNAPL), or depth to dense NAPL (DNAPL):

- Personal safety equipment (hard hat, steel-toed boots, safety vests, etc)
- Electronic water level meter (for water level measurements only)
- Interface probe (suitable for groundwater, LNAPL and DNAPL measurements)

- Photoionization detector (see *SOP 26 – • Photoionization Detector*)
- Field logbook and/or sampling forms
- Indelible ink pens
- Clipboard
- Decontamination solutions in dedicated squirt bottles
- Paper towels

3 METHODOLOGY

The wells to be gauged will be identified in the project planning documents. In the field, the sampling team must verify the list of wells to be sampled with the well number on the casing. Prior to opening the well, the condition of the well casing and pad should be noted on the sampling forms and in the field logbook (see *SOP 010 – Field Logbook*). If there is any damage, particularly any that threaten the integrity of the sampling point, the Project Manager and Field Team Leader should be notified immediately.

3.1 Depth to Groundwater Measurements

1. Open the well and monitor the headspace with the appropriate monitoring instrument to determine the presence of volatile organic compounds if there is information to suggest that volatiles may be present at levels to warrant an upgrade in the level of PPE. Record the measurement in the field logbook and/or sampling forms.

2. Locate the surveyed measuring point of the well. The surveyed measuring point location is typically the top of the inner well riser, and should be clearly marked in permanent ink on the well riser or identified in previous sample collection records. The measuring point location should be described in the Field Logbook and should be the same point used for all subsequent measurements.

3. To obtain a water level measurement, lower a decontaminated water level meter into the monitoring well. Care must be taken to assure that the water level measuring device hangs freely in the monitoring well and is not adhering to the wall of the casing. The water level measuring tape will be lowered into the well until the audible sound of the unit is detected or the light on an electronic sounder illuminates. At this time, the precise measurement should be determined (to one hundredth of a foot) by repeatedly raising and lowering the tape to converge on the exact measurement. The water level measurement should be entered in the Field Logbook and/or sample log sheets.

4. The water level measuring device shall be decontaminated in accordance with *SOP 16 – Equipment Decontamination* immediately after use. Generally, only that portion of the measuring tape which penetrates the water table will require decontamination. If NAPL is encountered, use of a solvent (*e.g.,* hexane) will be required to clean the probe before it is used in another well.

3.2 NAPL Measurements

NAPL measurements should be made using an interface probe. Interface probes are commonly used to detect the presence of any floating (LNAPL) or sinking (DNAPL) immiscible layers. These probes can also be used to measure the water levels inside wells.

1. Using the grounding cable attached to the interface probe, ground the probe to a metal object (*i.e.,* protective steel locking well cover) to prevent electric shock.

2. The probe should be lowered slowly inside each well. When LNAPL is detected, the probe will make a solid tone. Record the measurement from the surveyed point on the top of the well casing to the top of the LNAPL. Continue lowering the probe (observing the calibrated drop line) until the steady tone stops. When water is detected, the probe will make a beeping noise to signify the beginning of the water column. When the beeping noise is heard, observe the calibrated drop line to determine the water level. Record this measurement. The measurement on the drop line between when the steady tone began (*i.e.*, LNAPL was encountered) and when it stopped (*i.e.,* groundwater was encountered) will determine the apparent thickness of the LNAPL layer.

3. The depth to DNAPL can also be determined using the interface probe. Lower the probe through the water column to the bottom of the well. The probe will make a solid tone if a DNAPL is encountered. Record the depth to the top of the DNAPL layer, and the depth to the bottom of the well to determine the apparent thickness of the DNAPL layer.

4. The NAPL measuring device should be thoroughly cleaned after each use in accordance with the Sampling Equipment Decontamination SOP. If NAPL is encountered, use of a solvent (*e.g.,* hexane) will be required to clean the probe before it is used in another well.

4 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance and quality control for water level and NAPL measurements shall consist of several steps. First it is important to verify the well identification number, check transcription to the Field Logbook and/or sample log sheets, and ensure that the well is one that is included in the project planning documents as a point of interest.

Additional quality control measures include repetitive measurements of the depth to water or NAPL to ensure that accurate and precise results are obtained. Once the measuring device indicates that the water level or NAPL layer has been encountered, the probe should be raised slightly and lowered several times to check and confirm the measurement. A single final reading should be recorded in the field logbook or on the project specific form.

Water levels in piezometers and monitoring wells should be allowed to stabilize for a minimum of 24 hours after well construction and development, prior to measurement. Also, measurements should always be taken from the least to the most contaminated wells while decontaminating the equipment between each well.

If water level data are to be used for groundwater flow direction determination, all measurements should be taken within the shortest time frame feasible. Typically, this is within 24 hours; however, with large numbers of wells, one day may not be adequate.

5 DOCUMENTATION AND RECORD KEEPING

Proper field data collection and management is important. Data may either be entered into a bound field logbook or other form specified in a site-specific work plan, as described in *SOP 03 – Field Logbook*.

6 REFERENCES

United States Environmental Protection Agency, January 1991, Compendium of ERT Groundwater Sampling Procedures: Washington D.C**.,** EPA/540/P-91/007**.**

United States Environmental Protection Agency, September 1986, RCRA Ground-Water Monitoring Technical Enforcement Guidance Document: Office of Waste Programs Enforcement, Washington, D.C., EPA/530/SW-86/055

SOP No. 020
FIELD LOCATION OF SAMPLING POINTS
STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) specifies the procedure for translating proposed sample locations shown in work scopes to actual sample locations in the field. Actual sample locations will be recorded for entry into the ArcGIS database that EnviroAnalytics Group (EAG) has established to manage all data for the Sparrows Point Project. Proposed sample locations are shown in task work plans on CAD or ArcGIS drawings generated from the ArcGIS database. In many cases the proposed sample locations are specified to correspond to features observed on the geo-referenced plant drawings or historical aerial photographs. Therefore, the locations of these proposed sample locations must be translated from the work scope figures to the field to ensure that samples are collected in the proper locations to investigate the intended features. In some cases, sample locations must be adjusted in the field due to access restrictions, equipment refusal or based on field observations. In these cases, the revised sample locations must be recorded and entered into the ArcGIS database to ensure that the data from these samples are attributed to the correct locations on the site.

In most cases, a handheld Global Positioning System (GPS) devise will be utilized to acquire field sample locations and to record the actual sample locations.

1.1 Referenced SOPs

None

1.2 Definitions

(Reserved)

2 REQUIRED MATERIALS

Handheld GPS (Trimble GeoXH or equivalent)

3 METHODOLOGIES

3.1 Creating and Uploading Sample Point File onto GPS Unit

GPS Pathfinder Office Project Creation

- Open Windows Explorer to the correct project folder on the GIS Server (dropbox).
    - Within the GIS project folder, create a new folder titled *"Survey"*
        - Example: Dropbox_Projects\Rex Energy\13318-1-1-Adams Well Pad\GIS\Survey
- Open GPS Pathfinder Office
    - Create a new project for GPS Pathfinder Office Under *"Select Project"* then click *"New…"*
    - Project Name should be the official project name beginning with the project number and ending with the project/site name
        - Example: S13127-1-17-Friendsville Pipeli
        - ❖ **NOTE:** There is a character limit… put whatever fits.
    - Project Folder should be the path to the *"Survey"* folder
        - Example: \Dropbox_Projects\Keystone Clearwater\S13127-1-17-Friendsville Pipelines Permitting\GIS \Survey
    - Backup Folder should just have text *"Backup"*
    - Export Folder should just have text *"Export"*
    - Base File Folder should just have text *"Base"*
    - Click *"OK"* to create new project
        - A box will pop up stating folder already exists… click *"Yes"*
- ❖ **NOTE:** Never create additional folders within a survey folder. The only acceptable additional folders are phase/task/site, in that order. Do not organize data by date; it should be organized similarly to the project structure on the central server.
    - Within the *"Survey"* folder, GPS files may be stored within phases and tasks. Exported shapefiles may also be stored within phases and tasks inside the *"Export"* folder.
        - Example: Dropbox_Projects\ClientABC\S1234-1-1-Example Project\Survey\Phase 2\Task5
        - Example: Dropbox_Projects\ClientABC\S1234-1-1-Example Project\Survey\Export\Phase 2\Task5

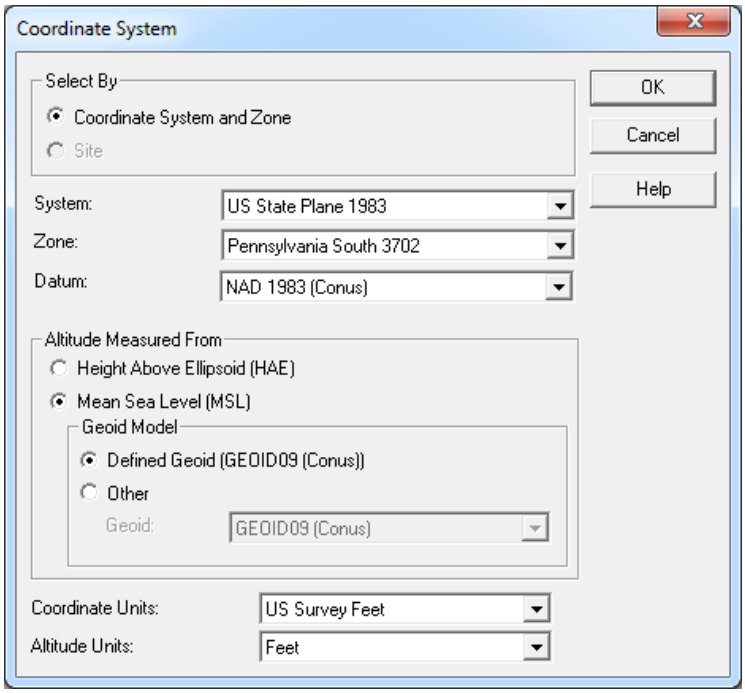
GPS File Naming

- GPS files should be stored under the *"Survey"* folder in the appropriate phases and tasks.
- Files must be named appropriately: (Date of Survey, Project Number, Project Name, Initials)
    - Example: 150122_13241-1-1-Adams_SLM

GPS File Creation

- Open ArcMap, set coordinate system and add shapefiles you want included in GPS file (SSF).
    - Coordinate system should match intended GPS coordinate system (NAD 83, PA South ft, PA North ft, etc.)
- Export all shapefiles to a temporary folder on desktop
    - When exporting the shapefiles, under *"Use the same coordinate system as:"* make sure to choose *"the data frame"*
        - This exports the shapefile with the correct coordinate system

- ❖ **NOTE:** You can skip the step above if you already have the shapefiles needed, and they are in the correct coordinate system.
- Open GPS Pathfinder Office and select the correct project – if you need help creating a project, reference *"GPS Pathfinder Office Project Creation"* section.
- Set the coordinate system in GPS Pathfinder Office
  - Click *"Options"* then *"Coordinate System."*
    - Below are the options you want selected:
      - Select By: Coordinate System and Zone
      - System: US State Plane 1983
      - Zone: Pennsylvania South (whatever state plane coordinate system you want to use)
      - Datum: NAD 1983 (Conus)
      - Altitude Measured From: Mean Sea Level (MSL)
        - Geoid Model: Definded Geoid
      - Coordinate Units: Us Survey Feet
      - Altitude Units: Feet
    - Then click *"OK"*



- Import shapefiles to be used in GPS file
  - Click *"Utilities"* then *"Import"*
    - Under *"Selected Files:"* click *"Browse…"*
      - Browse to the shapefiles you created in the temporary folder on your desktop

        - Select all the files and click *"Open"*
    - Under *"Output File:"* click *"Browse…"*
        - Browse to the project *"Survey"* folder and name the file appropriately – for correct naming convention, reference *"GPS File Naming"* section.
        - Under *"Save as type:"* select *"Imported files"* then click *"Save"*
        - All .IMP, .SSF and .COR file types should be saved in the *"Survey"* folder and then further broken down by phase/task/site when appropriate. Do not use dates to organize data. Use phases/tasks/sites.
    - Under *"Choose an Import Setup"* select *"Sample ESRI Shapefile Setup"*
    - Change coordinate system by selecting *"Properties"* then going to the *"Coordinate System"* tab
        - Select *"Change"*
        - Below are the options you want selected:
            - Select By: Coordinate System and Zone
            - System: US State Plane 1983
            - Zone: Pennsylvania South (whatever state plane coordinate system you want to use)
            - Datum: NAD 1983 (Conus)
            - Altitude Measured From: Mean Seal Level (MSL)
                - Geoid Model: Definded Geoid
            - Coordinate Units: Us Survey Feet
            - Altitude Units: Feet
        - Then click *"OK"*
        - ❖ **NOTE**: Even if the *"Import"* window shows the correct coordinate system, it **often is not actually correct**. This happens frequently... make sure you **double check.**
        - Click *"OK"* again, and then click *"OK"* once more to complete the import
- Open the *.imp file that you just created in Pathfinder Office.
    - Click *"File"* then *"Save As"*
        - The file should be named exactly as the .IMP
        - Under *"Save as type:"* you want to select *"Field data files (*.ssf)"*
        - Click *"SAVE"*
    - ❖ **NOTE:** If you want to use a data dictionary, reference the *"Data Dictionary"* section below. If you do not wish to use a data dictionary, move on to the next step
        - Some GPS units do not allow you to use a data dictionary
    - ❖ **NOTE:** Using a Data Dictionary is highly recommended.
- Now the GPS file (.SSF) is ready to be imported into the GPS unit

- At this point you want to double check and make sure your shapefiles are in the correct locations spatially
    - Open the shapefiles you loaded into a new ArcMap session
    - Also open the .SSF you created that contains those shapefiles within GPS Pathfinder Office
    - Now choose a specific point or corner of the shapefile in GPS Pathfinder Office as well as in ArcMap and make sure the coordinates shown are the same in both instances
    - If they are the same, you may now import the .SSF file to the GPS unit.

Adding a Data Dictionary to GPS File

- In order to add a data dictionary to your .SSF file, you must copy the existing data dictionary .IMP file to the same folder your .SSF file is located in.
    - Data Dictionary .IMP file location: Dropbox\GISDATA_Templates\Data Dictionary
- Now, select the *"Combine"* icon on the left hand side of the GPS Pathfinder Office screen 
    - Click *"Browse"* and select both the Data Dictionary .IMP file and the .SSF file you created
    - Click *"Open"*
    - Click *"Output File…"* and name your file appropriately. It should be exactly the same as the .SSF file, but add *"_DD"* to the end of the filename.
        - *"Save as type:"* should be *"Field data files (*.ssf)"* then click *"Save"*
    - Now click *"OK"* then *"OK"* and *"YES"* until your new .SSF file is created
    - Please DELETE your original .SSF file that does not include the Data Dictionary

Connecting GPS Unit to Computer

- Connect GPS unit to USB cable connected to your computer and turn the GPS unit ON
- Double check the date on the unit before transferring any files to the unit. If the unit battery died in the field, it will reset the date and this will mess up your files.
- Windows Mobile will eventually pop up on your computer screen when GPS unit is connected
    - Click *"Connect without setting up your device"*
        - You are now connected

Setting Coordinate System on GPS Unit

- When within TerraSync on the GPS unit, under the top left drop down select *"Setup"* then choose *"Coordinate System"*
- Below are the options you want selected
    - System: US State Plane 1983

- Zone: Pennsylvania South (whatever state plane coordinate system you want to use)
- Datum: NAD 1983 (Conus)
- Altitude Reference: Mean Seal Level (MSL)
- Altitude Units: Feet
- Coordinate Units: Us Survey Feet
- ❖ **NOTE:** you want to choose the same coordinate system you used to create the .SSF file.. which is also the same coordinate system as the shapefiles used to create the .SSF file.

Uploading GPS Files (.SSF) to GPS Unit

- Open the .SSF file you want uploaded within GPS Pathfinder Office
- Select the "Data Transfer" Icon on the left hand side of your screen 
- If the GPS unit is connected correctly, the green check mark should be automatically selected
  - If it is not automatically selected, try clicking the green check mark to connect it
- Select the *"Send"* tab, then the *"Add"* drop down, then *"Data File"*
  - Select the .SSF file you created.
  - If the GPS unit has a SD card installed, make sure you choose *"Storage Card"* as the *Destination* rather than *"Default"*
  - Click *"Open"*
  - Then click *"Transfer All"*
  - ❖ **NOTE:** it is **VERY** important to make sure the **GPS unit** is set with the correct coordinate system **before opening any files** loaded onto it. The coordinate system should be set exactly the same as the coordinate system you used when importing your shapefiles.
- At this point you want to double check and make sure your shapefiles are in the correct locations spatially.
  - ❖ **NOTE: This is a different step** than what you performed after creating the .SSF file.
  - Open the .SSF file within GPS Pathfinder Office
  - Also open the .SSF file within the GPS unit. When within TerraSync on the GPS unit, under the top left drop down select *"Map"*
  - Now choose a specific point or corner of the shapefile in GPS Pathfinder Office as well as on the GPS unit and make sure the coordinates shown are the same in both instances
  - If they are the same... CONGRATULATIONS, you have successfully uploaded your files!!

3.2 Navigating to Sample Points

1. Turn on the GPS by pushing the green power button at the bottom. The GPS touchscreen can be operated using your finger or the stylus provided.
2. Before going to the field, make sure that the GPS has a good battery charge. Press and hold the power button until the power menu appears. This will show the estimated run time in hours; we will get less time since we do real-time correction.
3. Tap the Microsoft Start icon and then the "TerraSync" icon. The TerraSync software is arranged in 5 Sections (upper left dropdown menu): Status, Map, Data, Navigation and Setup. Tap "Setup" from the section dropdown menu and under "Options" tap "Connect to GNSS" You will see an icon that looks like 2 pistons hitting each other, they will stop when the GPS receiver is connected. You will then see a blinking satellite icon near the top of the screen. The number to the left of this icon shows how many satellites are transmitting to the GPS. As more satellites connect, the icon will stop blinking and the GPS will be able to receive data.
4. The External DGPS Source (cellular data plan) will usually connect when you connect to GNSS, however, if it is not connected now then tap "Setup", "Options" and "Connect to External Source". You can tell that the external source is not connected 1) if you get an error message, 2) if the estimated GPS error is greater than usual or 3) by tapping the cellular status icon (top).
5. The estimated error is shown near the top; cm above a 2-sided arrow. When connected to the MSRN website (via our cellular plan) we expect an error of about 10cm.
6. Tap "Data" (section menu). Tap "New" and then "Existing File". This will bring up all preloaded files. Select the desired file and then "Open". The names of the point locations in that file will appear in a list on the screen. Slide the scroll bar to the right if you want to see the distance in meters that you are from each point.
7. Select the first point you will be navigating to and tap "Options" and then "Set Nav Target" from the pull down menu. Tap "Data" and then "Navigation" from the pull down menu.
8. Start moving. You will see a large circle with an arrow inside. The arrow indicates the direction to which you want to walk to get to the target. You must be moving to get accurate navigation information. The distance and direction to your target is shown at the bottom of the screen.
9. When you get to within 5 meters of your target the GPS will beep a few times and a small circle indicating the position of your target will appear in the middle of the screen. Also you will see a small "x" which indicates your position and will move as you move. Continue moving toward your target until the "x" is in the middle of the circle to indicate that you have reached your target.
10. To navigate to another point (target), tap the "Nav" button then "Data" and this will again bring up your list of point locations in the file. Proceed through steps 6-8 again until you have located all necessary points. "Close" the file when finished.

11. When you are finished, tap "Setup" then "Options" and select "Disconnect from GNSS". Tap "Exit" to close the TerraSync program.

12. When you return to the lab, plug the recharging cable into the GPS so the battery will be charged for its next use. Disconnect the GPS when a constant green light displays to show that the battery is fully charged. This will significantly increase the life of the battery.

3.3 Recording Actual Sample Points

1. Proceed through steps 1-5 in Section 3.2.
2. Tap "Data" then "New". Enter a file name.
3. Choose the desired data dictionary. Use the "KBS LTER" dictionary for predefined LTER features or the "Generic" dictionary for other features. Tap Create.
4. When using the KBS LTER data dictionary, it will list feature types (such as plot corner). Select a feature and tap the "Create" at bottom of screen. If using a generic data dictionary without predefined features, select point, and then tap "Create". You can add notes about the point.
5. Position yourself so that the GPS is over the feature and tap "Log" to start collecting GPS data for that feature.
6. As the GPS begins logging points you will hear a clicking sound and a number at the top right of the screen will increase with each logged point. A small bulls-eye icon to the left of the number will blink, indicating that data is being logged. Remain stationary until you have logged at least 30 points for your feature. Then tap "Done". Move to your next location and repeat.
7. When you are done collecting your locations tap "Close". This will save your file for later use.
8. When finished proceed to Steps 11-12 in Section 3.2.

3.4 Downloading Sample Point File from GPS Unit

GPS Pathfinder Office Project Creation

- Open Windows Explorer to the correct project folder on the GIS Server (dropbox).
  - Within the GIS project folder, create a new folder titled *"Survey"*
    - Example: Dropbox_Projects\Rex Energy\13318-1-1-Adams Well Pad\GIS\Survey
- Open GPS Pathfinder Office
  - Create a new project for GPS Pathfinder Office Under *"Select Project"* then click *"New…"*
  - Project Name should be the official project name beginning with the project number and ending with the project/site name
    - Example: S13127-1-17-Friendsville Pipeli
    - ❖ **NOTE:** There is a character limit… put whatever fits.
  - Project Folder should be the path to the *"Survey"* folder
    - Example: \Dropbox_Projects\Keystone Clearwater\S13127-1-17-Friendsville Pipelines Permitting\GIS \Survey

- Backup Folder should just have text *"Backup"*
- Export Folder should just have text *"Export"*
- Base File Folder should just have text *"Base"*
- Click *"OK"* to create new project
  - A box will pop up stating folder already exists… click *"Yes"*

❖ **NOTE:** Never create additional folders within a survey folder. The only acceptable additional folders are phase/task/site, in that order. Do not organize data by date; it should be organized similarly to the project structure on the central server.

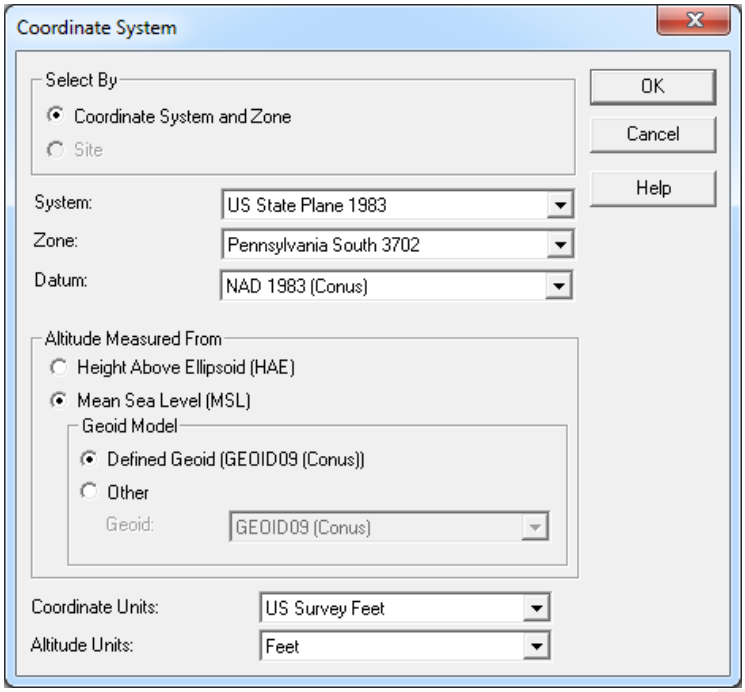
- Within the *"Survey"* folder, GPS files may be stored within phases and tasks. Exported shapefiles may also be stored within phases and tasks inside the *"Export"* folder.
  - Example: Dropbox_Projects\ClientABC\S1234-1-1-Example Project\Survey\Phase 2\Task5
  - Example: Dropbox_Projects\ClientABC\S1234-1-1-Example Project\Survey\Export\Phase 2\Task5

Connecting GPS Unit to Computer

- Connect GPS unit to USB cable connected to your computer and turn the GPS unit ON
- Windows Mobile will eventually pop up on your screen when GPS unit is connected
  - Click *"Connect without setting up your device"*
    - You are now connected

Downloading Un-Corrected Data from GPS Unit

- Open GPS Pathfinder Office and connect to the appropriate project – If you need help creating a project, reference *"GPS Pathfinder Office Project Creation"* section
- Connect GPS unit to your computer – if you need help connecting to your computer, reference *"Connecting GPS Unit to Computer"* section
- Set the coordinate system in GPS Pathfinder Office
  - Click *"Options"* then *"Coordinate System."*
    - Below are the options you want selected:
      - Select By: Coordinate System and Zone
      - System: US State Plane 1983
      - Zone: Pennsylvania South (whatever state plane coordinate system you want to use)
      - Datum: NAD 1983 (Conus)
      - Altitude Measured From: Mean Seal Level (MSL)
        - Geoid Model: Defended Geoid
      - Coordinate Units: Us Survey Feet
      - Altitude Units: Feet
    - Then click *"OK"*



- Select the *"Data Transfer"* Icon on the left hand side of your screen 
- If the GPS unit is connected correctly, the green check mark should be automatically selected
    - If it is not automatically selected, try clicking the green check mark to connect it
- Select the *"Receive"* tab, then the *"Add"* drop down, then *"Data File"*
    - Select the .SSF file you want to download and click *"Browse"* to select the appropriate destination for your file. You can do them individually if they are going to separate phases/tasks/site folders within the Survey folder.
        - ❖ **NOTE**: Several files are automatically selected; make sure you only select the files you want to download. Sorting by date modified may be best.
    - Then click *"Open"*
        - You can see what files you've selected by looking at the *"Files to Receive"* box
    - Then click *"Transfer All"*
        - If you get an error, go to the unit itself and make sure that the file is closed.

Correcting GPS Data – Downloading Base Files

- Open GPS Pathfinder Office and connect to the appropriate project and set your coordinate system
- Then open the .SSF file you want to post process.
- Now log onto www.keynetgps.com , selecting *"VRS Login"* and use the user info below
    - Organization: ARM GROUP INC

  - User Name: armgroup2
  - Password: armgroup
- From the homepage click *"Reference Data Shop"* then *"Start new order"* then *"Continuously Operating Reference Station (CORS)"*
- Locate project location, then zoom and identify triangulating stations.
  - **NOTE:** Preference is to use stations with sensor type *"Trimble NETR5"* or *"NETR9."* You can determine this by opening a second browser tab displaying the *"Sensor Map"* and selecting the station in question. Click the *"Info"* tab and look at the *"Sensor Type"*
- Choose the closest stations. Select at least 3.
- Once desired stations are highlighted on the right side scroll list, click *"Next: Time Selection"*
- Select date and time interval corresponding to the data you want to correct. You must select a timeframe that gives complete coverage of points collected by GPS user. It is best to give a buffer of an hour at the start and end times to ensure coverage. (You can find the correct date for the data by looking in pathfinder office under Differential Correction)
  - **NOTE:** GPS time is based off of Greenwich Mean Time, so you will need to add 5 hours to all of your start times
    - Don't forget to adjust for daylight savings time (add 4 hours when clocks are ahead).
  - *"Interval"* is 15 seconds
  - Click *"Next: Add to order"*
    - **NOTE:** If GPS data is spread over multiple days, you may use multiple orders to get the appropriate time frames for the data.
  - Review your order and if satisfied, click *"Next: Delivery Options"*
    - Select "Download the data" and *"file format"* should be *"RINEX 2.11"* then click *"Next: Generate Data"*
  - Once data is generated, click *"Next: Order Details"* then click *"Download"*
  - Open the file in WinZip and extract to the *"Base"* folder within your *"Survey"* folder
    - Add a new folder and make the title of it the date(s) the data is corresponding to

Example: Dropbox_Projects\PVR Partners\13245-1-1-PVR vs ULS Lawsuit\GIS\Survey\Base\20130927_28\

<u>Correcting GPS Data - Differential Correction Wizard</u>

- Select SSF file(s) to correct
- Click *"Next"*
- Select the following radio buttons:

    - Processing type: *Automatic Carrier and Code Processing*
    - H-Star Processing: *Use a single base provider*
- Click *"Next"*
- Correct Settings (will stay the same). Click *"Next"*
- Select the following radio buttons:
    - Base Data: Go to 3rd Radio button and Click *"Browse"*
        - Navigate to your Project GPS file location and find the BASE folder and the date folder you created. Select all of the .14o file(s). (You can use CTRL to select multiple files). Then click *"OPEN"*
    - Reference Position: *Use reference position from base files*
- Click *"Next"*
- Select the following radio buttons:
    - Output Folder: *Use the same folder as the input file*
    - Output File Name: *Create a unique filename based on the input filename*
- Click *"Start"*

Exporting Corrected Data to Shapefile

- Open GPS Pathfinder Office and connect to the appropriate project and set your coordinate system
- Then open the .COR file you want to export to shapefiles.
- Now open Windows Explorer and browse to the *"Survey"* folder.
    - Shapefiles are exported to the *"Export"* folder within the Survey folder.
- Within the *"Export"* folder, browse to the appropriate phase and task.
    - ❖ **NOTE:** If these are not yet set up, they need to be created. Use the folder structure on Dropbox/GIS Server or the main project folder as a template.
- Create a new Folder for the exported shapefiles. This folder should be named exactly the same as the .COR file you are exporting. Add "_COR" to the end of the file name to indicate these shapefiles are from a corrected GPS file.
- Within GPS Pathfinder office, Click "*Utilities,*" then *"Export."*
    - If your .COR file is not listed under the *"Selected Files"* below the "*Input Files"* section, browse to the .COR file and open it.
    - Next you want to browse to the *"Output Folder."* Exported shapefiles need to be saved in the *"Export"* folder. Browse to the folder you created previously.
        - Click *"OK"*
            - ❖ **NOTE:** Alternatively, you could browse to the appropriate folder within Windows Explorer and simply copy and paste the path under *"Output Folder"*
    - Make sure you have chosen *"Sample ESRI Shapefile Setup"* under *"Choose an Export Setup."*

- Then Click *"Properties"* and go to the *"Coordinate System"* tab. Make sure the appropriate coordinate system is selected.
  - ❖ **NOTE:** THIS IS VERY IMPORTANT: Even if it looks like the appropriate coordinate system is selected, often times it is not. You can double check by reading what the coordinate system is beside the *"Browse"* button. If you slide the text all the way to the left you can see what the coordinate system actually is. Do not rely on what is listed under the *"Use Current Display Coordinate System"* button.
  - Click *"OK"*
- Click *"OK"* and the shapefiles will be exported to the correct folder
- Open ArcMap, set coordinate system and add shapefiles you exported to ensure they are in the correct location.

Organize and Distribute Data for GIS and CAD

- Open exported shapefiles in ArcMap.
- Create the Sample Locations shapefiles
  - Shapefiles should be saved in a *"Sample Locations"* folder located at the following path: Project\GIS\Shapefiles\Sample Locations
  - Have scientist/data collector review shapefiles to make sure everything is correct
- Distribute the Sample Locations to CAD
  - Open Windows Explorer and browse to the following location: Project\Submissions\GIS to CAD
  - Create a *"Sample Locations"* folder if one isn't already created
    - Within this folder create a new folder named by today's date (YYYYMMDD)
      - Copy your wetland and stream shapefiles to this location

- Distribute all other GPS data
    - Open Windows Explorer and browse to the following location: Project\Submissions\GIS to CAD
    - Create a *"GPS Data"* folder if one isn't already created
        - Within this folder create a new folder named by today's date (YYYYMMDD)
    - Bring GPS data into ArcMap. Organize and export all data to the folder you just created.
        - You do not need to export the GPS data you used to create the Sample Locations shapefiles.
- Notify the CAD Designer when you are finished.

4 QUALITY ASSURANCE/QUALITY CONTROL

When the data are received, the complete files are reviewed prior to data entry. This step ensures that the data meet the project specifications with respect to accuracy and completeness. The final sample locations are plotted with the proposed locations to verify and note any changes to the proposed locations.

5 DOCUMENTATION AND RECORD KEEPING

All data are retained in electronic format in addition to being entered into the ArcGIS database. Original data CDs are kept in the file to support evaluation of any questions about the original data. Data are formatted into tables per the project manager's specific requirements.

6 REFERENCES

(Reserved)

SOP No. 021
IN-SITU HYDRAULIC CONDUCTIVITY TESTING STANDARD OPERATING PROCEDURE
Rev. 01

1 SCOPE

The purpose of this Standard Operating Procedure (SOP) text is to supply overall technical guidance for conducting permeability tests during hydrogeological studies. Pressure permeability tests using packers are not discussed in this SOP.

When determining hydraulic conductivity, it must be understood that disturbance to the formation during drilling operations will affect the data. Prior to performing any tests, the well in question should be adequately developed. Poor well efficiency, including inappropriate slot size and condition, as well as poor gravel pack condition could produce non-representative results.

1.1 Referenced SOPs

None

1.2 Definitions

Hydraulic Conductivity (K): A quantitative measure of the ability of porous material to transmit water. It is the volume of water that will flow through a unit cross-sectional area of porous material per unit time under a head gradient. Hydraulic conductivity is dependent upon properties of the medium and fluid. Hydraulic conductivity replaces the term "coefficient of permeability,"

Intrinsic Permeability (k): Intrinsic permeability is dependent only on the properties of the formation.

Transmissivity (T): A quantitative measure of the ability of an aquifer to transmit water. The product of the hydraulic conductivity multiplied by saturated thickness.

Rising-Head Test: A test used in an individual borehole or well within the saturated zone to estimate the hydraulic conductivity of the surrounding formation by lowering the water level in the boring or well and measuring the rate of recovery of the water level. Another term for rising-head is a "bail test."

Falling-Head Test: A test used in an individual borehole or well to estimate the hydraulic conductivity of the surrounding formation by raising the water level in the boring or well and measuring the rate of drop in the water level. This test is also known as a "variable head test."

Constant-Head Test: Water is constantly added to the borehole or well to be tested, and the flow rate that is required to maintain a hydraulic head at a constant level above the static water level is measured. In the unsaturated zone, water is added to the borehole to maintain the certain water depth until outflow from the borehole into the soil or rock has become essentially constant.

Slug Test: A form of rising- or falling-head test. A slug consisting of a solid cylinder or quantity of water of known volume is added or removed from the boring or well to be tested. The cylinder of known volume acts to raise or lower the water level in the well. The rate of rise or drop in the water table is measure
d.

Unconfined Aquifer: An aquifer in which the water table is in direct contact with the atmosphere.

Confined Aquifer: An aquifer that is overlain and underlain by strata of lower permeability.

2 REQUIRED MATERIALS

- Solid slug of known volume
- Weighted tape of suitable length or electronic water level meter
- Pressure transducer
- Data logger
- Field logbook
- Indelible ink pens

3 METHODOLOGIES

3.1 Using a Pressure Transducer and Data Logger

Become familiar with the operation of the data logger before going to the field. Also, make sure that it has a full charge and sufficient available memory for data storage.

Prepare the equipment and the well for the hydraulic conductivity test.

- Decontaminate all down-hole equipment which will come in contact with groundwater, in accordance with *SOP 16 – Equipment Decontamination*.
- For each pressure transducer: enter its calibration constants (provided by the manufacturer) into the data logger. Check the calibration by lowering the transducer in the well to 5 feet below the static water level measured by hand-held water level probe; raise 1 foot at a time, recording the transducer reading at each 1-foot interval to the water surface. This procedure will serve as a well-specific calibration and an operational test of the transducer.
- Install pressure transducers in the pumping well and observation wells to the desired depths, and secure transducer cable firmly to well head.
- Measure and record distance from the top of the well casing (TOC) to the measuring point on transducer.

- Measure the pre-test water level in all wells (extraction and observation wells) after equilibration of water levels.
- Input setup parameters into data logger(s) per manufacturer's instructions and initiate collection of monitoring data from the transducers.

3.2 In-Situ Hydraulic Conductivity Testing in Borings

In-situ hydraulic conductivity testing performed in the borehole permit testing of formations at various depths throughout the drilling process. The boreholes should be drilled using casing, allowing the investigation of discrete intervals. The most appropriate testing method is dependent on type of drilling, geologic, and general site conditions. Various testing methods are discussed below.

Both rising head and falling head hydraulic conductivity tests can be performed in saturated formations during drilling operations. Various methods are used in conducting these tests. One method consists of performing the test through the bottom of the borehole. This method is accomplished as follows:

1. Advance the borehole to the desired testing depth.
2. Set the casing flush with the bottom of the borehole.
3. Clean the hole out, to remove loose materials, and slowly withdraw the drilling equipment.
4. Add a few feet of sand, possessing a higher permeability than the surrounding formation, to the bottom of the borehole.
5. Once the water level in the borehole has stabilized, the static water table should be measured from a fixed position on the casing and recorded.
6. Refer to Section 3.1 for the installation and use of a transducer.
7. Raise (falling-head test) or lower (rising-head test) the water level and measure the change in water level elevation at the desired time intervals measured by the pressure transducer. The test should be conducted until the water level stabilizes or for a minimum of 30 minutes. In low permeability formations, it is sometimes impractical to run the test until stabilization of the water level is reached.

The second method utilizes a temporary well with a 5 to 10 foot screen. This procedure is accomplished as follows:

1. Place the screened well into the cleaned-out boring, pulling the drilling casing back to expose the screen.
2. Allow the formation to collapse around the screen (or place a sand/gravel pack around the screen should the formation not collapse).
3. The hydraulic conductivity test should be performed as described earlier.

This method allows for testing of a larger portion of the aquifer resulting in more reliable hydraulic conductivity estimates.

Another testing method is the constant head test. The constant head test is suitable for use in unsaturated as well as saturated conditions. In this method, water is added to the boring at a

measured rate, which is sufficient to maintain a constant head above the static water level. The discharge rate is recorded over a period of time (10 to 20 minutes) after a stable elevated water level has been reached. This is the most accurate of the methods discussed, and should be given preference when materials are available to perform the test. At the completion of the test, additional data may be obtained in saturated formations by measuring the rate of drop in water level in the boring.

3.3 In-Situ Hydraulic Conductivity Testing in Wells

The above-mentioned tests may also be performed in completed wells. Prior to testing, the well should be thoroughly developed and allowed to stabilize in order to obtain more accurate results. Slug tests may be performed in completed wells. In a slug test, a known volume of water is displaced in the well by either introducing or removing a solid cylinder or quantity of water of known volume. The procedure for performing a slug test is as follows:

1. Allow the water level in the well to stabilize, and measure the static level.
2. Refer to Section 3.1 for the installation and use of a transducer.
3. Instantaneously introduce the solid cylinder or quantity of water into a well under static conditions using a fast, smooth action. Measure the change in water level elevation over time, using the pressure transducer.
4. Allow the water level to return to static, and remove the slug with a relatively fast, smooth action (slug-out test). If water is used as a slug, instantaneously remove a bail of water from a well under static conditions and measure the change in water level with respect to time.

The slug-out test should be utilized with preference over the slug-in test, as it produces more accurate results. In the slug-in test, interference is created by the introduction of the slug into the water, whereas in the slug-out test, interference is minimal.

In addition to time and depth measurements, the following data should also be recorded:

- Ground elevation
- Reference elevation
- Depth of test run
- Inside casing diameter
- Length of uncased borehole
- Equipment used
- Riser pipe, screen diameter, and lengths
- Screen slot size
- Sand/gravel pack porosity or grain size
- Procedures used

3.4 Data Reduction

Various methods of data reduction are available to calculate the permeability and hydraulic conductivity of the tested aquifers. The type of method used is dependent on the hydrogeologic conditions encountered. The following methods commonly used include:

- Bouwer and Rice Method
- Cooper et. al. Method
- Hvorslev Method

These methods are not discussed within this text. Many other aquifer specific methods are available and should be consulted.

4 QUALITY ASSURANCE/QUALITY CONTROL

All calculations are to be performed by a licensed professional geologist. All calculations shall be checked and included in the project files.

5 DOCUMENTATION AND RECORD KEEPING

All test results, field logbooks, and field forms are to become part of the permanent project files.

6 REFERENCES

Cooper, H.H. Jr., Bredehoeft, J. and Papadopulos, I.S., 1967, Response of a Finite-Diameter Well to an Instantaneous Charge of Water: , v. 3:1, p. 263-269.

Bouwer, H. and Rice, R.C., 1976, A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells: Water Resources Research, v. 12:3,p. 423-428.

Hvorslev, J.M, April 1951, Time Log and Soil Permeability in Groundwater Observations: U.S. Army Corps of Engineers Bulletin No. 36.

SOP No. 022
AQUIFER PUMPING TESTS
STANDARD OPERATING PROCEDURE
Rev. 01

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1 SCOPE

The Standard Operating Procedure (SOP) describes equipment and procedures used when conducting aquifer pumping tests. This SOP does not discuss pumping test design, or the evaluation of pumping test data, which are dependent on site-specific factors. For discussion regarding pumping test design and comprehensive pumping test analysis methods, refer to Driscoll (1986), Stallman (1971), Walton (1970), or other published and peer-reviewed sources

Aquifer pumping tests are used to define hydrogeologic properties of an aquifer, including the capacity of an aquifer to transmit and store water, and possible boundary effects.

1.1 Referenced SOPs

SOP 016 – Equipment Decontamination

1.2 Definitions

(Reserved)

2 REQUIRED MATERIALS

The following equipment is to be used for performing aquifer pump tests:

- Groundwater pump of appropriate type and capacity (usually a submersible pump or centrifugal pump)
- Hand-held (electronic) water level probe
- Flow meter
- Calibrated bucket
- Discharge piping and/or hose with adjustable in-line valve
- Pressure transducers and electronic data logger(s)
- Stop watch
- Log-log or semi-log graph paper or portable computer with spreadsheet program
- Flashlight (if necessary)
- Rain gauge
- Barometer or barometric pressure transducer
- Effluent-water container (*e.g.,* Baker Tank), if necessary

- Generator or other power source with proper gauge electrical wire extension
- Field logbook and indelible ink pens
- Personal protective equipment, as needed

3 METHODOLOGIES

The following steps are essential to the performance of a pumping test:

1. Become familiar with the operation of the data logger before going to the field. Also, make sure that it has a full charge and sufficient available memory for data storage.

2. Prepare the equipment and the well for the aquifer test through performance of the following activities:

    - Decontaminate all down-hole equipment which will come in contact with groundwater, in accordance with *SOP 016 – Equipment Decontamination*.
    - For each pressure transducer: enter its calibration constants (provided by the manufacturer) into the data logger. Check the calibration by lowering the transducer in the well to 5 feet below the static water level measured by hand-held water level probe; raise 1 foot at a time, recording the transducer reading at each 1-foot interval to the water surface. This procedure will serve as a well-specific calibration and an operational test of the transducer.
    - Install pressure transducers in the pumping well and observation wells to the desired depths, and secure transducer cable firmly to well head.
    - Measure and record distance from the top of the well casing (TOC) to the measuring point on transducer.
    - Install the submersible pump, or the suction hose intake for a surface pump, in the extraction well; secure the pump, or intake, at the desired depth above the transducer, but below the estimated maximum drawdown level.
    - Measure the pre-test water level in all wells (extraction and observation wells) after equilibration of water levels.
    - Measure and record the distance from the pumping well to the observation wells.
    - Input setup parameters into data logger(s) per manufacturer's instructions and initiate collection of monitoring data from the transducers.

3. Perform an equipment shakedown by checking the performance of each piece of testing equipment. Included in the shakedown should be:

    - Verify that the groundwater pump can pump steadily at the anticipated testing rates.
    - Check the calibration of the flow meter by performing manual flow tests, using a calibrated container of known volume (usually a 5-gallon bucket) and a stop watch.

4. If necessary, monitor water levels under static (non-pumping) conditions to determine natural trends in water levels. Among the continuously monitored observation wells should be at least one observation well which is believed to lie out of the zone of influence of the pumping test well; see Section 4.0 for further augmentation of this procedure.

5. If necessary, perform a step-drawdown test to estimate the optimum pumping rate for the constant discharge longer term aquifer pumping test. The step-drawdown test is performed by pumping the extraction well at 3 to 5 different discharge rates for approximately 1 to 2 hours at each step, increasing the discharge rate for each step, and monitoring the resulting water levels in the pumping well and selected observation wells. Using the step test results, estimate the optimum flow rate for the constant discharge test.

   After the step-drawdown test is performed and water levels have returned to approximate pre-test levels, examine the recovery data for any factors that may have influenced the water level readings during the test such as tidal effects or pumping of nearby well(s). If these are significant, collect an additional 24 hours of antecedent trend water level data (for all wells including the background well) while determining (if possible) the cause and the magnitude of the sources of interference. If influencing factors are not detected, start the constant rate discharge test. The flow rate during the constant rate test will be determined from the results of the step-drawdown test.

6. Perform the following activities prior to and during performance of the constant rate drawdown test:

   - Prior to discharge, measure the water levels of selected observation wells to identify static water level conditions.
   - Record all necessary data and zero the transducers.
   - At the start of the discharge tests, water level measurements are to be collected continuously using pressure transducers and data logger(s).The frequency of measurements recorded by the data logger(s) will decrease throughout the test. Data are to be collected at the maximum possible frequency during the first few minutes of the test and less frequently during the later stages of the test. Collect enough readings for all parts of each log cycle.
   - The discharge rate is to be held constant to the greatest extent possible, and checked at regular intervals after the start of the test. Flow rate will be adjusted as necessary to maintain a constant rate. The flow rate and total discharge volume (incremental and cumulative) are to be recorded periodically.
   - During the course of the pumping test, measurements are to be graphically plotted on log-log graph paper (*via* computer spreadsheet) to examine the drawdown curve. Plotting the data will enable the supervising hydrogeologist to identify when the testing objectives have been met, and when the discharge phase of the pumping test should be stopped.

7. At the termination of the drawdown test, the pump is to be shut off (at an accurately documented time) and the data logger(s) reset to record the water level recovery. Recovery measurements are to be made using the same recording schedule as was used for the drawdown data. Recovery monitoring is to continue for approximately 24 hours or until water levels have recovered by at least 90 percent of the test drawdown.

4 QUALITY ASSURANCE/QUALITY CONTROL

In addition to the above mentioned items, the following field activities are to be performed in support of the aquifer tests to insure that the test data are usable.

1. Prior to and during the aquifer test, the following meteorological data is to be collected; or, if the data are available, the information may be obtained from a local weather station:

    - Temperature
    - Rainfall frequency and intensity
    - Barometric pressure

2. Effluent groundwater is to be discharged to an on-site water treatment system (if available) or to holding tanks.

3. If necessary, samples of the groundwater discharge are to be collected according to proper protocol at regular time intervals for chemical analysis.

4. The water level in at least one observation well outside of the apparent cone of depression is to be monitored for large-scale (*e.g.*, "background") water level fluctuations that may influence the test results. If necessary, the test results may then be corrected for "background" fluctuations. If antecedent trend data have been taken, the correction factors can be determined by comparing background well responses to antecedent trend results for the aquifer being corrected. Such fluctuations may result from barometric pressure effects, diurnal gravitational cycles (earth tides), groundwater recharge, or other natural or anthropogenic effects.

5. Prior to and during the performance of the pumping test, observe and record any other conditions which may affect interpretation of the pumping test results. Such conditions may include variations of flow in nearby streams, flood events, or interruptions in pumping for any reason.

Pumping test data evaluation will be dependent on the specific data needs of each test as well as the response of the hydraulic system. Non-ideal conditions such as partially penetrating wells, leaky aquifers, and unconfined aquifers influence the technique(s) used to evaluate the aquifer response data. Software programs which facilitate evaluation of the data may be used; however, these programs should not be used as a substitute for professional judgment.

The following methods of pumping test analysis may be employed to evaluate aquifer hydrogeologic properties. This list includes only a partial overview; detailed pumping test evaluation is discussed in several references.

- Steady-state determination (for validation of other methods)
- Distance-drawdown, to calculate the radius of influence of the pumping well (semi-logarithmic straight-line plot)
- Jacob Straight-Line Method (to calculate aquifer transmissivity [T], storativity [S], and boundary effects)

- Theis Curve-Matching Method and/or Hantush-Jacob Curve-Matching Method (to calculate T, S, and leakance parameters, if indicated)
- Neuman Curve-Matching Method (to calculate T and S in unconfined aquifers)
- Image-well analysis (to determine limits on zone-of-influence by boundaries)

5 DOCUMENTATION AND RECORD KEEPING

All calculations are to be documented and checked by a senior geologist familiar with the methodologies used. All calculations are retained in both paper and electronic format in the project files.

6 REFERENCES

Driscoll, F.G., 1986, Groundwater and Wells - 2nd Edition: St. Paul, Minnesota: Johnson Screens, 1089 p.

Stallman, R.W., 1971, Aquifer-test design, observation and data analysis: Techniques of Water Resources Investigations of the U.S. Geological Survey, Ch. B1: Washington, D.C.: U.S. Government Printing Office.

Walton, W.C., 1970, Groundwater Resource Evaluation: New York: McGraw-Hill, Inc., 664 p.

SOP No. 023
XRF PROCEDURES
STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) identifies the methods used for performing lead-based paint inspections to determine whether lead-based paint is present in a building, and which building components contain lead-based paint. This SOP also addresses the use of the XRF for field screening analysis of metals in soils.

Portable XRF lead-based paint analyzers are the most common primary field analytical method because of their demonstrated abilities to determine if lead-based paint is present on many surfaces and to measure the paint without destructive sampling or paint removal, as well as their high speed and low cost per sample. Portable XRF instruments expose a building component to X-rays or gamma radiation, which causes lead to emit secondary X-rays with a characteristic frequency or energy. The intensity of this radiation is measured by the instrument. The inspector must then compare this displayed value (reading) with the inconclusive range or threshold specified in the *XRF Performance Characteristic Sheet* for the specific XRF instrument being used, and the specific substrate beneath the painted surface.

2 EQUIPMENT

XRF Instrument (INNOV-X Systems Alpha Series XRF Spectrometer)

XRF Performance Characteristic Sheet

3 SAMPLE LOCATIONS

The selection of the test location for a specific testing combination should be representative of the paint over the areas which are most likely to be coated with old paint or other lead-based coatings. Thus, locations where the paint appears to be thickest should be selected. Locations where paint has worn away or been scraped off should not be selected. Areas over pipes, electrical surfaces, nails, and other possible interferences should also be avoided if possible. All layers of paint should be included and the XRF probe faceplate should be able to lie flat against the surface of the test location.

If no acceptable location for XRF testing exists for a given testing combination, a paint-chip sample should be collected. The sample should include all paint layers and should be taken as unobtrusively

as possible. Because paint chip sampling is destructive, a single sample may be collected from a wall and used to characterize other walls with the same testing combinations, i.e. the same overlying paint layers and underlying surface materials.

4 PROCEDURES FOR PAINT TESTING

4.1 Number of XRF Readings for Each Testing Combination

XRF testing is required for at least one location per testing combination, except for interior and exterior walls, where four readings should be taken, one on each wall. Multiple readings on the same testing combination or testing location are unnecessary in other circumstances.

4.2 XRF Instrument Reading Time

The recommended time to open an XRF instrument's shutter to obtain a single XRF result for a testing location depends on the specific XRF instrument model and the mode in which the instrument is operating. The *XRF Performance Characteristic Sheet* provides information on this issue. To ensure that a constant amount of radiation is employed for instruments requiring manual adjustment of the open-shutter time must be increased as the source ages and the radiation source weakens. Almost all commercially available XRF instruments automatically adjust for the age of the source (operators should check with manufacturers of instrument). The following formula should be employed for instruments requiring manual adjustment:

$$\text{Open-Shutter Time} = \text{Nominal Time} * 2^{(\text{Age}/\text{Half-life})}$$

4.3 General Procedures

1. The inspector will use the MDE guidelines for determining whether paint is considered to be lead-based. The Maryland State Regulations for XRF equipment consider paint containing greater than 0.7 mg/cm^2 to be lead-based, or above 0.5% by weight according to laboratory results. The HUD/EPA standard for lead-based paint, as defined by Title X of the 1992 Housing and Community Development Act, is less stringent (1.0 mg/cm^2 or 0.5%) and thus will be disregarded. The MDE standard which defines a lead-based paint applies to both homes and other buildings, and thus is used in this context.
2. Obtain the *XRF Performance Characteristic Sheet* for the X-Ray Fluorescence (XRF) lead paint analyzer to be used in the inspection. It will specify the ranges where XRF results are positive, negative or inconclusive, the calibration check tolerances, and other important information. Contact the National Lead Information Center Clearinghouse (1-800-424-LEAD) to obtain the appropriate *XRF* Performance Characteristic Sheet, or download it from the Internet at www.hud.gov/lea/leahome.html.

3. Report lead paint amounts in mg/cm^2 because this unit of measurement does not depend on the number of layers of non-lead-based paint and can usually be obtained without damaging the painted surface. All measurements of lead in paint should be in mg/cm^2, unless the surface area cannot be measured or if all paint cannot be removed from the measured surface area. In such cases, concentrations may be reported in weight percent (%) or parts per million by weight (ppm).
4. Take at least three calibration check readings before beginning the inspection. Additional calibration check readings should be made every 4 hours or after inspection work has been completed for the day, or according to the manufacturer's instructions, whichever is most frequent. Calibration checks should always be done before the instrument is turned off and again after it has been warmed up (calibration checks do not need to be done each time an instrument enters an automatic "sleep" state while still powered on).
5. For each building or surface inspected, identify all testing combinations. A testing combination is characterized by the component type, paint type, and the substrate (underlying surface). Certain building components that are adjacent to each other and not likely to have different painting histories can be grouped together into a single testing combination. Painted surfaces include any surface coated with paint, shellac, varnish, stain, paint covered by wallpaper, or any other coating. Any wallpaper encountered should be assumed to cover paint unless building records or physical evidence indicates otherwise.
6. Take at least one individual XRF reading on each testing combination. For rooms within a larger structure, take a minimum of four readings (one reading on each wall). A different visible color does not by itself result in a separate testing combination.
7. Determine whether to correct the XRF readings for substrate interference by consulting the *XRF Performance Characteristic Sheet*. If test results for a given substrate fall within the substrate correction range, take readings on that bare substrate scraped completely clean of paint.
8. Classify XRF results for each testing combination. Readings above the upper limit of the inconclusive range are considered positive, while readings below the lower limit of the inconclusive range are considered negative. Readings within the inconclusive range (including its boundary values) are classified as inconclusive. Some instruments have a threshold value separating ranges of readings considered positive from readings considered negative for a given substrate. Readings at or above the threshold are considered positive, while readings below the threshold are considered negative.
9. All inconclusive readings must be confirmed in the laboratory, unless it is assumed that all inconclusive results are positive. Such an assumption may reduce the cost of an inspection, but it will probably increase subsequent abatement, interim control, and maintenance costs, because laboratory analysis often shows that testing combinations with inconclusive readings do not in fact contain lead-based paint. Inconclusive readings cannot be assumed to be negative. Make classifications of all testing combinations or component types in the structure as a whole, based on the proportions of positive, negative, and inconclusive results.

10. The inspector should write an inspection report indicating if and where lead-based paint is located in the unit or building. The inspection report should contain detailed information on the following:
    - Who performed the inspection;
    - Date(s) of inspection;
    - All XRF readings;
    - Specific information on the XRF and laboratory methodologies;
    - Building or structure information and sampling location identifiers;
    - Results of any laboratory analyses: and
    - Classification of all surfaces into positive or negative categories (and final determinations for any inconclusive readings), based on XRF and laboratory analyses.

5 PROCEDURES FOR SOIL TESTING

5.1 General Procedures

1. Several NIST certified standards are provided with the XRF meter and can be used to check the instrument's accuracy. Prior to using the XRF meter in the field, at least one standard should be measured for a minimum of one minute. It is highly recommended that more standards should be measured if there are multiple elements of interest at a site. Standards come in sample cups that have both a solid cap and a Mylar window. The soil sample should be measured through the Mylar window on a test stand, if available. Do not hold the cup while the XRF is reading, or else the operator will be exposed to X-ray radiation. If no test stand is available, the cup should be placed on the ground and the meter should be pointed downward, while in full contact with the cup. The results displayed by the XRF should be within ±20% of the value of the standard if accurate measurement has been achieved.
2. For in-situ testing, ensure that the testing site has soil that is easily accessed and not covered by grass and rocks. The front of the probe head should be directly contacting the ground and should remain that way while the reading is being taken. Between a sampling at each site, be sure to clean the analyzer window of dirt to retain accuracy.
3. For testing a prepared sample, usage of a testing stand is highly recommended and the sample should entirely cover the window of the stand. The operator should not hold the sample while the XRF is running, else they are exposing themselves to X-ray radiation. Samples analyzed by this method should be compacted and have a minimum thickness of 0.5 inches in order to retain accuracy of results. Samples should also be as uniform and homogeneous as possible.
4. To begin a test, use the XRF's trigger or press start on the screen of the accompanying smart device. The red warning light at the top of the instrument will blink when the testing has

begun and confirms the emittance of X-rays from the XRF. After a short amount of time set by the user, intermediate data will appear on the screen of the XRF and can be freely scrolled through. However, the testing will continue until the maximum time range, also set by the operator, has passed. All results will be available on the screen and can be freely scrolled through.

6 QUALITY ASSURANCE/QUALITY CONTROL

6.1 XRF Calibration Check Readings

In addition to the manufacturer's recommended warm up and quality control procedures, the XRF operator should take the quality control readings recommended below, unless these are less stringent than the manufacturer's instructions. Quality control for XRF instruments involves readings to check calibration. Most XRFs cannot be calibrated on-site; calibration can only be accomplished in the factory.

6.1.1 Frequency and Number of Checks

For each XRF instrument, two sets of XRF calibration check readings are recommended at least every 4 hours. The first is a set of three nominal-time XRF calibration check readings to be taken before the inspection begins. The second occurs either after the day's inspection work has been completed, or at least every 4 hours, whichever occurs first. To reduce the amount of data that would be lost if the instrument were to go out of calibration between checks, and/or if the manufacturer recommends more frequent calibration checks, the calibration check can be repeated more frequently than every 4 hours. If the XRF manufacturer recommends more frequent calibration checks, the manufacturer's instructions should be followed. Calibration should be checked before the XRF is turned off and after it is turned on again.

6.1.2 Interpreting Calibration Check Readings

A successful calibration check should be obtained before additional XRF testing is conducted. Readings not accompanied by successful calibration checks at the beginning and end of the testing period are unreliable and should be repeated after a successful calibration check has been made. If a backup XRF instrument is used as a replacement, it must successfully pass the initial calibration check test before retesting the affected test locations. This procedure assumes that the HUD/EPA lead-based paint standard of 1.0 mg/cm^2 is being used, although the separate MDE building standard is used in this case. At this time, no method for determining performance characteristics using different standards has been developed.

7 SAMPLE ANALYSIS

XRF results are classified as positive, negative, or inconclusive.

If the reading gathered from the XRF instrument is less than the lower boundary of the inconclusive range, or less than the threshold of the XRF Performance Characteristic Sheet for the specific XRF instrument and specific substrate beneath the painted surface, then the reading is considered negative. If the reading is greater than the upper boundary of the inconclusive range, or greater than or equal to the threshold, then the reading is considered positive. Readings within the inconclusive range, including its boundary values, are considered inconclusive. An inconclusive classification indicates that the XRF cannot determine with reasonable certainty whether lead is present on the testing combination. All inconclusive results should be confirmed by laboratory analysis, unless the client wishes to assume that all inconclusive results are positive.

A positive classification indicates that lead is present on the testing combination at or above the MDE standard of 0.7 mg/cm^2 (or 0.5% by weight). A negative classification indicates that lead is not present on the testing combination at or above the standard. Because the inconclusive ranges and/or thresholds shown in the *Performance Characteristic Sheet* are based on the HUD/EPA standard (1.0 mg/cm^2), readings and analytical results must be compared to the MDE standard for identification and disclosure purposes.

8 REFERENCES

U.S. Department of Housing and Urban Development. *Guidelines for the Evaluation and Control of Lead-Based Paint Hazards in Housing.* Rep. Washington D.C.: U.S. Department of Housing and Urban Development, 1997

Maryland Department of the Environment. *Maryland Lead Paint Abatement Regulations (COMAR 26.02.07).* 1988, Amended 1996, 2003, 2004. <http://www.dsd.state.md.us/COMAR/ComarHome.html>

SOP No. 024
ELECTRONIC DATA DELIVERABLES FOR LABORATORY ANALYTICAL DATA STANDARD OPERATING PROCEDURE
Rev. 01

1 SCOPE

This Standard Operating Procedure (SOP) specifies the formatting requirements for the submission of electronic laboratory analytical data.

Attachment 1 presents the file layout structure for the "Labdata.dbf" file.

1.1 Referenced SOPs

None

1.2 Definitions

(Reserved)

2 REQUIRED MATERIALS

All work is to be conducted using ARM Group's network.

3 METHODOLOGIES

(Reserved)

4 QUALITY ASSURANCE/QUALITY CONTROL

When the data is received, the complete files are reviewed, including the results of the quality control samples and field duplicates. This step ensures that the data meet the project specifications with respect to accuracy and completeness.

5 DOCUMENTATION AND RECORD KEEPING

All data is retained in electronic format and in hard copy. Original data CDs are kept in the file to support any regulatory questions about the original data. Data is formatted into tables per the project manager's specific requirements, e.g., organized by chemical, medium, date, or other criteria to support discussion of the nature and extent of impacts or the development of risk assessments, remedial actions, etc. Comparison to remedial action or regulatory requirements can also be performed by the data manager or project personnel.

6 REFERENCES

(Reserved)

ATTACHMENT 1
GIS ELECTRONIC DATA DELIVERABLES
FILE LAYOUT

Remark	Justify	Field Name	Type	Description
lab	L	Site	Text	Sparrows Point
lab	L	Station ID	Text	Identifier for Area of Site that sample was collected from
lab		Lab Sample ID	Text	Laboratory generated identification for the sample
lab	L	Client Sample ID	Text	Client assigned identification for the sample
lab		Matrix	Text	Sample matrix, e.g. soil, groundwater, air, water
lab	L	Sample Type	Text	Grab or composite sample
lab		Date Collected	Date/ Time	Date (and time) the sample was collected in the field
lab	L	Percent Moisture	Number	A measure of the moisture content of the sample, generally used for soil samples
lab		Analysis Method	Text	The analytical method perform on the sample, e.g. TO-15, SW846 8260B.
lab	L	Dilution Factor	Number	The multiplier by which sample was diluted.
lab	L	Analysis Date	Date/ Time	Date of the analytical run.
lab		CAS	Text	The registry number assigned to the analyte by the Chemical Abstract Services may also be populated with codes for analytes that do not have official CAS numbers
lab		Analyte	Text	Generally the IUPAC name for the analyte
lab		Result	Number	The amount of the analyte detected in the sample
lab		Final Result	Number	The result after any potential adjustment through data validation
lab		Unit	Text	The unit of measure the result is reported in

Remark	Justify	Field Name	Type	Description
lab	L	Flag	Text	A alphanumeric flag assigned by the laboratory, used to qualify the reported result
lab	L	VFlag	Text	A flag added during the data validation process, used to qualify the reported result
lab	L	Final Flag	Text	The flag used taking into consideration laboratory and data validation qualifiers
lab	L	Detect	Text	Indicates whether the reported result should be treated as a detection
lab	L	Useable?	Text	Indicates whether, after the data validation process, the data is considered useable
lab		High Limit	Number	This is the reporting limit
lab	L	High Limit Type	Text	RL or QL or PQL
lab	L	Low Limit	Number	This is the limit of detection
lab	L	Low Limit Type	Text	MDL
lab	R	Percent Recovery	Number	Populated only for LCS, MS and MSD
lab	L	Lower Recovery	Number	Populated only for LCS, MS and MSD. This indicates the lower acceptance limit for the QA
lab	L	Upper Recovery Limit	Number	Populated only for LCS, MS and MSD. This indicates the upper acceptance limit for the QA sample
lab	L	RPD	Number	Populated only for MS and MSD. Indicates the relative percent difference between MS and MSD
lab	L	RPD Limit	Number	Populated only for MS and MSD. Indicates the acceptable limit for RPD between MS and MSD.
lab	R	Receipt Lab	Text	The analytical laboratory that initially received the samples

Remark	Justify	Field Name	Type	Description
lab	R	Project Description	Text	A user generated descriptor for the project
lab	L	SDG	Text	The laboratory sample delivery group
lab	L	Lab Job ID	Text	Identifier assigned to the project by the laboratory
lab	R	COC ID	Text	Identifier for Chain of Custody
lab	L	Sample Type Desc	Text	Descriptor for Sample Type, e.g. FB (field blank), FD (field duplicate)
lab	L	Date Received	Date/ Time	Date (and time) the samples were received and logged in by the laboratory
lab	L	Total Sample Amount	Number	Volume or Mass of sample
lab	L	Total Sample Amount Unit	Text	The unit of measure the total sample amount is reported in
lab	L	Leach Batch	Text	identifier for all laboratory analytical leachate batches
lab	L	Leach Method	Text	Laboratory Leachate method name or description (If leachate is required)
lab	L	Leach Date	Date/ Time	Beginning date (and time) of leachate preparation (Required if the sample is leached)
lab		Prep Batch	Text	Identifier for all laboratory analytical preparation batches
lab	L	Prep Method	Text	Sample preparation method code
lab		Prep Date	Date/ Time	Date (and time) sample preparation began
lab		Prep Type	Text	Description of the preparation method, e.g. extraction, filtering.
lab		Initial Amount	Number	The initial sample aliquot used in the prep/extraction process

Remark	Justify	Field Name	Type	Description
lab	L	Initial Amount Unit	Text	The unit of measure for the initial sample aliquot
lab	L	Final Amount	Number	The final amount of the prep digestate/distillate
lab	L	Final Amount Unit	Text	The unit of measure for the final amount of prep digestate/distillate
lab		Re-analysis Type	Text	Descriptor for reanalysis (if any), e.g. DL (dilution), RE (re-extract), DL2 (second dilution), RE2 (re-extract 2)
lab		Analysis Batch	Text	The batch identifier assigned by the laboratory to represent a group of samples run on an instrument.
lab		Analysis Lab	Text	Name of Laboratory performing the analysis
lab		Instrument ID	Text	Laboratory ID for the instrument used in the analysis
lab		Column/Detector ID	Text	Laboratory ID for the type of column or detector used in the analysis
lab		Basis	Text	Basis for reporting (DRY or WET or NA)
lab	L	Analyte Type	Text	Indicates if the reported analyte is a target (TRG) or a surrogate (SUR) recovery
lab	L	Result Status	Text	Primary or confirmation
lab	L	Decision Level	Text	Indicates the level of data validation
lab	L	Retention Time (TIC)	Text	Log of the retention time if a tentatively identified compound is recovered
lab	L	Spike Amount	Number	The concentration, adjusted for prep aliquots, analytical dilution factors, and percent moisture wherever applicable, of the spike added for surrogates, tracers, LCS, LCSD, MS, MSD, ICVs, CCVs, post spikes, etc. Required for spiked analytes.
lab	L	Expected Amount	Number	The acceptable percent recovery range of the spiked amount in accordance with method specifications

SOP No. 025
NIOSH METHOD 6009 SAMPLE COLLECTION STANDARD OPERATING PROCEDURE
Rev. 02

1 SCOPE

This Standard Operating Procedure (SOP) identifies the equipment and techniques used in the collection of air or soil gas samples to be analyzed for mercury (elemental) that will be collected using individual sorbent tube sampling trains, each consisting of an air sampling pump and sorbent tube. Sorbent tube sampling trains used for sampling ambient air will be allowed to sample over a period of approximately four (4) hours at 0.15 to 0.25 L/min for a total sample size between 2 and 100 L. Each sampling pump and sorbent tube train will be set to a method-specific flow rate in the field at the time each sample is started.

Air or soil gas samples for elemental mercury analysis will be collected if the analysis of total mercury in soil or groundwater indicates a potential for vapor intrusion.

2 EQUIPMENT

2.1 Required Equipment

- An **air sampling pump** capable of sampling at the recommended flow rate with the sampling medium in line, such as:
  - SKC 210 Series Pocket Pump®
  - SKC 224-XR Universal Series Sampler with Adjustable Flow Holder Cat. No. 224-26 Series
  - SKC AirChek® 2000 Sampler with Constant Pressure Controller Cat. No. 224-26-CPC and Adjustable Flow Holder Cat. No. 224-26 Series
  - SKC AirChek 52 Sampler with Constant Pressure Controller Cat. No. 224-26-CPC and Adjustable Flow Holder Cat. No. 224-26 Series
  - SKC 222 Series Low Flow Sampler
- An **air flow calibrator,** such as:
  - SKC UltraFlo® Calibrator Cat. No. 709
  - DC-Lite Flowmeter 717 Series
- The **sorbent sample tube** specified in the method
- The **appropriate tube holder** or protective tube cover

2.2 Optional Equipment

- SKC **Tube Breaker** Cat. No. 222-3-50 (for 6- and 7-mm OD tubes) or 222-3-51 (for 8- and 10-mm OD tubes)

3 PROCEDURES

Air sampling pumps will consist of SKC AirCheck XR5000 units supplied SKC, Inc. ("SKC") of Eighty Four, Pennsylvania. Each pump will be paired with a method-specific sorbent tube and pre-set with a specific flow rate setting for the respective tube method (e.g., mercury). Pumps that are adjusted for each tube method will be affixed with a label indicating that flow adjustments have been pre-set. At the time of deployment at each sampling location, each pump will be flow calibrated using a DCLite Flowmeter supplied by SKC. Flow calibration, flow readings, and start times for each sorbent tube sampling train will be recorded onto a pump calibration form in the field. The flow rate will also be checked at the end of sampling. Sampling pumps will be flow-calibrated and started individually around approximately the same time. After a sampling period of approximately 4-hours, the sampling pumps will then be flowchecked and shut down to conclude the sampling for each pump and tube sampling train. Sorbent tube sampling, including pump calibration, tube preparation and flow check, will be performed. The basic procedures for collecting a sorbent tube sample for each individual tube method are as follows:

- Record the current sampling location on the appropriate field forms (include map ID and/or GPS coordinates)
- Connect a representative sampler tube (e.g., acetaldehyde) to be used for flow calibration to the DC-Lite flowmeter. Connect the flowmeter to the XR5000 air pump pre-set for the respective tube method.
- Calibrate sampling pump with the representative sampler and flow meter in line. Label the pump, noting the parameter to be sampled. Adjust pump to desired flow rate and record the flow rate onto the Air Sampling Pump Calibration Log. Remove the sorbent tube and set aside for post sampling flow rate verification.
- Break the ends off a new sorbent tube immediately prior to sampling. Attach sorbent tube to pump with flexible tubing. Make sure that the tube matches the parameter labeled on the pump. Record start time onto the Air Sampling Pump Calibration Log.
- Sample at an accurately known flow rate for four hours. The sample flow rate can be determined at the end of sampling, while the pump is running, or after shutdown if the flow rate has not been changed.
- Cap the sorbent tube and pack securely for shipment with bagged refrigerant. DO NOT shut down the pump at this time. Each tube should go in a labeled Ziploc bag, noting sample ID and parameter, date and time. Labels should be prepared in such a way that they will not be ruined by water or refrigerant. Samples may be stored at 4C until they are shipped. Record the sampling information onto the Chain of Custody form.
- Using the same setup as for initial calibration, measure the flow rate again with the same dedicated sorbent tube specific to the pump used for that method. Record the final flow rate onto the Air Sampling Pump Calibration Log.

Specific sorbent tube methods to be used for the sampling and analysis program for this project are summarized below. These methods are published by the National Institute for Occupational Safety and Health ("NIOSH"), the Occupational Safety and Health Administration ("OSHA"), and U.S. EPA. The complete method descriptions associated with the proposed sorbent tube testing to be conducted for this project are readily-available from the above sources. NIOSH Method 6009 will

be used for analysis of mercury. The standard operating procedure for this method's sample collection is summarized as follows:

- Calibrate each personal sampling pump with a representative sampler in line. Record flow rate.
- Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
- Sample at an accurately known rate of 0.15 to 0.25 L/min for a total sample size between 2 and 100 L.
- Cap sampler and pack securely for shipment.
- Using a flow meter, calibrate the flow rate again with the same representative sampler. Record final flow rate.

4 QUALITY ASSURANCE/QUALITY CONTROL

All data must be documented on field data sheets or within field logbooks. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment calibration activities must occur prior to sampling/operation, and they must be documented.

Once samples have been placed into the appropriate sample containers, sample ID, sample location, and sample date and time of collection should be recorded on the sample label. This information shall be consistent with what is recorded on the chain-of-custody (COC).

The sample container(s) should be packaged in the laboratory-provided shipping container or box and transported to the laboratory, under COC protocol. The samples require no preservation and the holding time is 28 days at room temperature.

Field samples should be collected as required per the project work plan or project planning documentation.

5 REFERENCES

Soil Water Air Protection Enterprise. Quality Assurance Project Plan (QAPP) for Air Sampling Activities at the Bridgeton Sanitary Landfill in Bridgeton, Missouri. Rep. Santa Monica: Soil Water Air Protection Enterprise, 2013.

AIR SAMPLING PUMP CALIBRATION LOG

Bridgeton Sanitary Landfill Air Quality Assessment

COMPLETED BY: _____ PERSONNEL: _____

DATE: _____

PAGE: _____ of _____

CALIBRATION INSTRUMENT : _____

INITIAL PUMP SETUP (PRE-SAMPLING FLOW CHECK)

Sample ID	Analyte	SKC Tube ID	Air Pump Serial No.	START		END	
				Flow Rate (L/min)	Time (24 Hour)	Flow Rate (L/min)	Time (24 Hour)
e.g. acetaldehyde	e.g. acetaldehyde	e.g. 226-120	e.g. 123456				

NOTES / LOCATION REFERENCES

SOP No. 026
PHOTOIONIZATION DETECTOR (PID) STANDARD OPERATING PROCEDURE
Rev. 01

1 SCOPE

The purpose of this Standard Operating Procedure (SOP) is to describe the procedure for using a photoionization detector (PID). The PID is a portable, nonspecific, vapor/gas detector employing the principle of photoionization to detect a variety of chemical compounds, both organic and inorganic, in air.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

2 EQUIPMENT

- PID (MiniRAE 3000)
- Operating manual
- Battery charger for PID
- Spare batteries
- Tygon tubing
- Field Data Sheets/Site Logbook
- Intake assembly extension
- Strap for carrying PID
- Teflon tubing for downhole measurements
- Gear for protecting the PID from moisture and dirt e.g. protective case or plastic bags
- Isobutylene standards for calibration

3 METHOD SUMMARY

The PID is a useful general survey instrument at hazardous waste sites. A PID is capable of detecting and measuring real-time concentrations of many organic and inorganic vapors in air. A PID is similar to a flame ionization detector (FID) in application; however, the PID has somewhat broader capabilities in that it can detect certain inorganic vapors. Conversely, the PID is unable to

respond to certain low molecular weight hydrocarbons, such as methane and ethane, which are readily detected by FID instruments.

The PID employs the principle of photoionization. The analyzer will respond to most vapors that have an ionization potential less than or equal to that supplied by the ionization source, which is an ultraviolet (UV) lamp. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and form a positive ion. This will occur when the ionization potential of the molecule in electron volts (eV) is less than the energy of the photon. The sensor consists of a sealed ultraviolet light source that emits photons with an energy level high enough to ionize many trace organics, but not enough to ionize the major components of air (e.g., nitrogen, oxygen, carbon dioxide). The ionization chamber exposed to the light source contains a pair of electrodes, one a bias electrode, and the second the collector electrode. When a positive potential is applied to the bias electrode, an electro-magnetic field is created in the chamber. Ions formed by the adsorption of photons are driven to the collector electrode. The current produced is then measured and the corresponding concentration displayed on a meter, directly, in units above background.

Gases with ionization potentials near to or less than that of the lamp will be ionized. These gases will thus be detected and measured by the analyzer. Gases with ionization potentials higher than that of the lamp will not be detected. Ionization potentials for various atoms, molecules, and compounds are given in Table 1 (Appendix A of EPA SOP #2114). The ionization potential of the major components of air, oxygen, nitrogen, and carbon dioxide, range from about 12.0 eV to about 15.6 eV and are not ionized by 9.8 eV, 10.6 eV, or 11.7 eV lamps.

Table 2 (Appendix A of EPA SOP #2114) illustrates ionization sensitivities for a large number of individual species when exposed to photons from a 10.2 eV lamp. Applications of each probe are included in Table 3 (Appendix A of EPA SOP #2114).

4 INTERFERENCES AND POTENTIAL PROBLEMS

4.1 PID Instrument Limitations

1. The PID is a nonspecific total vapor detector. It cannot be used to identify unknown substances; it can only roughly quantify them.
2. The PID must be calibrated to a specific compound, typically isobutylene unless otherwise specified in the Work Plan.
3. The PID does not respond to certain low molecular weight hydrocarbons, such as methane and ethane.
4. Certain toxic gases and vapors, such as carbon tetrachloride and hydrogen cyanide, have high ionization potentials and cannot be detected with a PID.
5. Certain models of PID instruments are not intrinsically safe.

6. Electrical power lines or power transformers may cause interference with the instrument and thus cause measurement errors. Static voltage sources such as power lines, radio transmissions, or transformers may also interfere with measurements.
7. High winds and high humidity will affect measurement readings.
8. This instrument is not to be exposed to precipitation (rain). The units are not designed for this service.
9. Do not use this instrument for head space analysis where liquids can inadvertently be drawn into the probe.

4.2 Regulatory Limitations

Transport of calibration gas cylinders by passenger and cargo aircraft must comply with International Air Transport Association (IATA) Dangerous Goods Regulations or the U.S. Code of Federal Regulations, 49 CFR Parts 100-177. A typical calibration gas included with a PID is isobutylene. It is classified as a non-flammable gas, UN #1556 and the proper shipping name is Compressed Gas. It must be shipped by cargo aircraft only.

5 PROCEDURES

The sections below are in reference to the MiniRAE 3000 PID Meter, and are subject to change if a different PID instrument is used or specified in the Work Plan. If such an instance were to occur, the instrument's user guide or operations manual would be the primary source of procedure related information.

5.1 Preparation

Check out and ensure the proper operation of the PID, as appropriate, using the equipment checklist and user guide provided.

5.2 Start-Up Procedures

The instrument is designed as a broadband volatile organic compound(VOC) gas monitor and datalogger for work in hazardous environments. It gives real-time measurements and activates alarm signals whenever the exposure exceeds preset limits. Prior to factory shipment, the instrument is preset with default alarm limits and the sensor is pre-calibrated with standard calibration gas. However, you should test the instrument and verify the calibration before the first use. After the instrument is fully charged and calibrated, it is ready for immediate operation.

1. With the instrument turned off, press and hold [MODE].
2. When the display turns on, release the [MODE] key.

3. The RAE Systems logo should appear first. (If the logo does not appear, there is likely a problem and you should contact your distributor or RAE Systems Technical Support.) The instrument is now operating and performs self-tests. If any tests (including sensor and memory tests fail), refer to the Troubleshooting section of the user guide.
4. Once the startup procedure is complete, the instrument shows a numerical reading screen with icons. This indicates that the instrument is fully functional and ready to use.

5.3 Field Operation

1. All readings are to be recorded in the site logbook. Readings should be recorded, following background readings, as "units above background," not ppm.
2. As with any field instrument, accurate results depend on the operator being completely familiar with the operator's manual. The instructions in the operating manual should be followed explicitly in order to obtain accurate results.
3. Position the probe assembly close to the area to be monitored because the low sampling rate allows for only very localized readings. Under no circumstances should the probe tip assembly be immersed in fluid.
4. While taking care to prevent the PID from being exposed to excessive moisture, dirt, or contamination, monitor the work activity as specified in the site Health and Safety Plan. The PID survey should be conducted at a slow to moderate rate of speed and the intake assembly (the probe) slowly swept from side to side. There is a three to five second delay in read-out depending upon the instruments sensitivity to the contaminant.
5. During drilling activities, PID monitoring should be performed at regular intervals downhole, at the headspace, and in the breathing zone. In addition, where elevated organic vapor levels are encountered, monitoring may be performed in the breathing zone during actual drilling. When the activity being monitored is other than drilling, readings should emphasize breathing zone conditions.
6. When the activity is completed or at the end of the day, carefully clean the outside of the PID with a damp disposable towel to remove any visible dirt.

5.4 Post Operation

1. Press and hold the Mode key for 3 seconds. A 5-second countdown to shutoff begins.
2. Once the countdown stops, the instrument is off. Release the Mode key.
3. When you see “Unit off...” release your finger from the [MODE] key. The instrument is now off.
4. Complete logbook entries, verifying the accuracy of entries and signing/initialing all pages.
5. Check the equipment, repair or replace damaged equipment, and charge the batteries.

5.5 Equipment Calibration

5.5.1 Standard Two-Point Calibration (Zero & Span)

1. Press and hold [MODE] and [N/-] until you see the Password screen.
2. In Basic User Level, you do not need a password to perform calibrations. Instead of inputting a password, enter calibration by pressing [MODE]. **Note:** If you inadvertently press [Y/+] and change any of the numbers, simply press [MODE] and you will be directed to the calibration menu.

The Calibration screen is now visible with Zero Calibration highlighted.
These are your options:

- Press [Y/+] to select the highlighted calibration (Zero Calib or Span Calib).
- Press [MODE] to exit calibration and return to the main display and resume measurement.
- Press [N/-] to toggle the highlighted calibration type.

5.5.1.1 Zero (Fresh Air) Calibration

This procedure determines the zero point of the sensor calibration curve. To perform a fresh air calibration, use the calibration adapter to connect the instrument to a "fresh" air source such as from a cylinder or Tedlar bag (optional accessory). The "fresh" air is clean, dry air without organic impurities and an oxygen value of 20.9%. If such an air cylinder is not available, any clean ambient air without detectable contaminants or a charcoal filter can be used.

At the Zero Calibration menu, you can proceed to perform a Zero calibration or bypass Zero calibration and perform a Span calibration. You may also go back to the initial Calibration menu if you want to exit calibration.

- Press [Y/+] to start calibration.
- Press [MODE] to quit and return to the main calibration display.

1. Turn on your Zero calibration gas.
2. Press [Y/+] to start calibration

During the zeroing process, the instrument performs the Zero calibration automatically and does not require any action on your part. When Zero calibration is complete The instrument will then show the Calibration menu on its display, with Span Calib highlighted.

5.5.1.2 Span Calibration

This procedure determines the second point of the sensor calibration curve for the sensor. A cylinder of standard reference gas (span gas) fitted with a 500 cc/min. flow-limiting regulator or a

flow-matching regulator is the simplest way to perform this procedure. Choose the 500 cc/min. regulator only if the flow rate matches or slightly exceeds the flow rate of the instrument pump. Alternatively, the span gas can first be filled into a Tedlar bag or delivered through a demand-flow regulator. Connect the calibration adapter to the inlet port of the instrument, and connect the tubing to the regulator or Tedlar bag.

Another alternative is to use a regulator with >500 cc/min flow but allow the excess flow to escape through a T or an open tube. In the latter method, the span gas flows out through an open tube slightly wider than the probe, and the probe is inserted into the calibration tube.

At the Span Calibration menu, you perform a Span calibration. You may also go back to the Zero calibration menu or to the initial Calibration menu if you want to exit calibration.

- Press [Y/+] to enter Span calibration.
- Press [N/-] to skip Span calibration and return to Zero calibration.
- Press [MODE] to exit Span calibration and return to the top calibration menu.

If you have pressed [Y/+] to enter Span calibration, then you will see the name of your Span gas (the default is isobutylene) and the span value in parts per million (ppm).

1. Turn on your span calibration gas.
2. Press [Y/+] to initiate calibration.

During the Span calibration process, there is a 30-second countdown and the instrument performs the Span calibration automatically. It requires no actions on your part. The instrument then exits Span calibration and shows the Zero calibration menu on its display. When you are done performing calibrations, press [MODE], which corresponds with "Back" on the display. The instrument updates its settings and then returns to the main display. It begins or resumes monitoring.

6 QUALITY ASSURANCE

1. All data must be documented on field data sheets or within site logbooks.
2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

7 REFERENCES

Environmental Protection Agency. *Photoionization Detector (PID)* (1994): *EPA*. Environmental Protection Agency, 06 Oct. 1994. <http://www.dem.ri.gov/pubs/sops/wmsr2114.pdf>.

MiniRAE 3000 User Guide

PID CALIBRATION LOG

PROJECT NAME:	SAMPLER NAME:	
PROJECT NUMBER:	DATE:	PAGE ____ of ____

DATE/TIME	PID SERIAL #	FRESH AIR CAL	STANDARD	STANDARD CONCENTRATION	METER READING	COMMENTS
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
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			Isobutylene	100 ppm		
			Isobutylene	100 ppm		
			Isobutylene	100 ppm		

SOP No. 027
TURBIDIMETER
STANDARD OPERATING PROCEDURE
Rev. 03

1 SCOPE

The purpose of this standard operating procedure (SOP) is to provide a framework for calibrating turbidimeters used to measure the water quality parameter of turbidity for groundwater and surface water. This SOP supplements, but does not replace, EPA analytical methods listed in 40 CFR 136 and 40 CFR 141 for turbidity.

This SOP is written for instruments that measure turbidity.
Hach 2100 and 2100Qis Turbidity Meter
LaMotte 2020 we-wi Turbidimeter
LaMotte Turbidity Kit

For groundwater monitoring, turbidity is not measured conventionally like other water quality parameters. It must not be measured in a flow-through-cell because the flow-through-cell acts as a sediment trap. Instead, a groundwater sample should be collected and be measured in an environment free of interference from other light sources. This procedure is applicable for use with the *EPA Region I Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells.*

2 HEALTH AND SAFETY WARNINGS

Read all labels on the standards and note any warnings on the labels. Wear appropriate personal protection equipment (e.g., gloves, eye shields, etc.) when handling the standards. If necessary, consult the Material Safety Data Sheets (MSDS) for additional safety information on the chemicals in the standards.

3 GENERAL

All monitoring instruments must be calibrated before they are used to measure environmental samples. Most turbidimeters have different types of calibrations that can be performed, mainly two-point and three-point calibration. Some turbidimeters also have one-point calibration capability, but generally, these types of calibrations are less accurate than the two-point and three-point variant. Most often, the preferred method is the two-point calibration.

Most projects will require at least two standards to bracket the expected measurement range. This means that one standard is less than the expected value and one is higher. In the case of a three-point calibration, the third standard is often approximately equal or near the expected value and proves to be useful in increasing accuracy of the reading.

This SOP requires that the manufacturer's instruction manual (including the instrument specifications) accompany the instrument into the field.

4 PROCEDURES

4.1 Frequency of Calibration

At a minimum, the instrument is calibrated prior to use on the day the measurements are to be performed. A post calibration check at the end of the day is performed to determine if the instrument drifted out of calibration. Some projects may require more frequent calibration checks throughout the day in addition to the check at the end of the day. For these checks, the instrument can be recalibrated during the day if the instrument drifted out of calibration and only the data measured prior to the check would need to be qualified. The calibration/post calibration data information is recorded in Table 1.

Ideally, the temperature of the standards should be close to the temperature of the ambient water that is being measured.

4.2 Calibration Procedures

Prior to calibration, all instrument optics and cable connections must be cleaned and the battery checked according to the manufacturer's instructions. Failure to perform these steps (proper maintenance) can lead to erratic measurements.

The volume of the calibration solutions must be sufficient to fit inside the cuvette of sample (see manufacturer's instructions for the volume to be used).

Check the expiration date of the standards. Do not use expired standards.

All standards are stored according to manufacturer instructions.

The turbidity method is based upon a comparison of intensity of light scattered by a sample under defined conditions with the intensity of light scattered by a standard reference suspension. A turbidimeter is a nephelometer with a visible light source for illuminating the sample and one or

more photo-electric detectors placed ninety degrees to the path of the light source. Note: the below calibration procedure is for a turbidimeter which the sample is placed into a cuvette.

Some instruments will only accept one standard. For those instruments, the second, third, etc., standards will serve as check points.

1. Allow the calibration standards to equilibrate at the ambient temperature. The use of commercially available polymer primary standards (AMCO-AEPA-1) is preferred; however, the standards can be prepared using Formazin (read the warning on the label before use) according to the EPA analytical Method 180.1. Other standards may be used if they can be shown that they are equivalent to the previously mentioned standards.
2. If the standard cuvette is not sealed, rinse a cuvette with deionized water. Shake the cuvette to remove as much water as possible. Do not wipe dry the inside of the cuvette because lint from the wipe may remain in the cuvette. Add the standard to the cuvette.
3. Before performing the calibration procedure, make sure the cuvettes are not scratched and the outside surfaces are dry and free from fingerprints and dust. If the cuvette is scratched or dirty, discard or clean the cuvette respectively. Note: some manufacturers require the cuvette to be orientated in the instrument in a particular direction for accurate reading.
4. Select a low value standard such as a zero or 0.02 NTU and calibrate according to manufacturer's instructions. Note: a zero standard (approximately 0 NTU) can be prepared by passing distilled water through a 0.45 micron pore size membrane filter.
5. For most turbidimeters, select a high standard and calibrate according to manufacturer's instructions or verify the calibration if instrument will not accept a second standard. In verifying, the instrument should read the standard value to within the specifications of the instrument. If the instrument has variety of ranges, calibrate each range on that instrument with a standard that falls within that range, but not near its extremes.
6. Record the calibration information on Table 1.

4.3 Operation Procedures

Prior to operation, all instrument optics and cable connections must be cleaned and the instrument should be calibrated according to the manufacturer's instructions as well as those mentioned earlier in this SOP. Failure to perform these steps (proper maintenance and calibration) can lead to erratic measurements.

The volume of the water samples must be sufficient to fit inside the cuvette of sample (see manufacturer's instructions for the volume to be used).

1. Once the turbidimeter is powered on, wait for the main menu to appear. From the main menu select “Measure” or some variant thereof to have the device prepare to take a reading.
2. If turbidity values are expected to be less than 10 NTU, place a blank 0 NTU sample in the meter first, aligning the index line on the tube or cuvette with the meter’s index arrow. Once

that has been read, the meter will signal such. Afterwards, in a separate tube or cuvette that has been wiped down with a lint free cloth, the sample should be placed in the meter in the same fashion as the blank. The meter will then take a reading for 1 second after the user presses the button to initiate the command "Scan Sample". The reading will then appear on the screen.

3. If turbidity values are expected to be greater than 10 NTU, wipe down the sample's tube or cuvette with a lint free cloth to avoid unwanted residue that could tamper with result. Then, place the sample in the meter, aligning the index line on the tube or cuvette with the meter's index arrow. The meter will then take a reading for 1 second after the user presses the button to initiate the command "Scan Sample". The reading will then appear on the screen.

4.4 Post-Operation Calibration Check

After the initial calibration is performed, the instrument's calibration may drift during the measurement period. As a result, it is necessary to determine the amount of drift that occurred after collecting the measurements. This is performed by placing the instrument in measurement mode (not calibration mode) and placing the probe in one or more of the standards used during the initial calibration; for turbidity place the standard in a cuvette and then into the turbidimeter. Wait for the instrument to stabilize and record the measurement (Table 1). Compare the measurement value to the initial calibration value. This difference in value is then compared to the drift criteria or post calibration criteria described in the quality assurance project plan or the sampling and analysis plan for the project. If the check value is outside the criteria, then the measurement data will need to be qualified.

If the quality assurance project plan or the sampling and analysis plan do not list the drift criteria or the post-calibration criteria, use the criteria below.

Measurement	Post Calibration Criteria
Turbidity	± 5% of standard

Note: * Table 8.1, USEP A Region 1 *YSI 6-Series Sondes and Data Logger SOP,* January 30, 2007, revision 9.

5 DATA MANAGEMENT AND RECORD MANAGEMENT

All calibration records must be documented in the project's log book or on a calibration log sheet. At a minimum, include the instrument manufacturer, model number, instrument identification number (when more than one instrument of the same model is used), the standards used to calibrate the instruments (including source), the calibration date, the instrument readings, the post calibration check, and the name of the person(s) who performed the calibration. An example of a calibration log sheet is shown in Table 1.

6 REFERENCES

EPA Region I Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells.

Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998.

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

Turbidity - Methods for the Determination of Inorganic Substances in Environmental Samples,

EP A/600/R-93/100, August 1993.

USEPA Region 1YSI6-Series Sondes and Data Logger SOP, January 30, 2007, revision 9:

USGS Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting, Techniques and Methods 1-D3.

Turbidity Methods and Measurement, EPA Guidance Manual: Turbidity Provisions, April 1999.

TABLE 1
TURBIDIMETER CALIBRATION LOG

Project Name_____ Date_____
Weather_____

Calibrated by_____ Instrument_____
Serial Number_____

Parameters	Morning Calibration	Morning Temperature	End of Day Calibration Check*	End of Day Temperature
Turbidity Standard #1				
Turbidity Standard #2				
Turbidity Standard #3				

* For each Parameter, chose one standard as your check standard. If possible, choose the one that is closest to the ambient measurement value.

SOP No. 028
DIRECT PUSH INSTALLATION AND CONSTRUCTION OF TEMPORARY GROUNDWATER SAMPLE COLLECTION POINTS STANDARD OPERATING PROCEDURE
Rev. 01

1 SCOPE

This Standard Operating Procedure (SOP) provides procedures for the proper installation and construction of temporary Direct Push (DP) Groundwater Sample Collection Points (GSCP) in unconsolidated formations.

Installation of a DP-GSCP is minimally intrusive and causes less disturbance of the natural formation than standard installation techniques. Percussion-hammer Direct Push systems (e.g. Geoprobe) are smaller and thus more mobile and have more access to a site than traditional drill rigs. Sampling and data collection are faster, reducing the time needed to complete an investigation and increasing the number of sample points that can be collected during the investigation.

DP-GSCPs are used for many purposes: collection of groundwater for chemical analysis; measurement of groundwater levels; and detection of free-phase constituents. Regardless of their intended use, DP-GSCPs should be constructed to ensure the following:

- Good hydraulic connection is established between the well and the water-bearing zone of interest;
- Water from separate zones or aquifers are not interconnected, and well construction activities do not facilitate cross-contamination;
- Well construction activities do not alter the chemical characteristics of the aquifer;
- The well is properly sealed to prevent entry of surface water; and
- The well is properly identified.

2 EQUIPMENT

Equipment and materials used for the installation and construction of DP-GSCPs in unconsolidated formations will depend upon the subsurface conditions and anticipated depth to water. Based upon the chosen methods, the DP subcontractor will be responsible for providing a DP rig, support equipment, and trained crew capable of performing the requested installation and construction

activities. The qualified DP subcontractor will typically know, based on experience, what equipment will be required for specific situations. It is necessary, therefore, to provide the DP subcontractor with as much information as possible regarding the requirements and objectives for the installation and construction of the DP-GSCP, as well as the anticipated subsurface conditions.

Besides the general equipment necessary to create the borehole, the DP subcontractor will also obtain and provide the required materials for the DP-GSCPs. Material specifications will be the responsibility of the overseeing field personnel or project manager. The specifications are dependent upon anticipated subsurface conditions. The process by which the proper materials are selected is presented in the following section.

DP-GSCP construction materials typically will include the following:

- Temporary casing
- Well screen
- Riser pipe (to extend from the screen to the surface)
- Sand
- Sealing materials (bentonite chip, granular bentonite, potable water, etc.)
- Caps

In addition to the equipment and material needs of the DP subcontractor, the field manager overseeing the DP-GSCP construction activities will require particular items to assist in documenting construction activities. Equipment and materials likely to be used by oversight personnel may include:

- Field logbook and indelible ink pens
- Personal protective equipment (PPE) as prescribed in the Health and Safety Plan (HASP)
- Digital camera
- Weighted tape, pvc pipe or center ("control") rod for measuring borehole depths and DP-GSCP construction material placement
- Tape measure and/or ruler
- Water-level and/or interface probe

3 PROCEDURES

The site-specific or project-specific Health and Safety Plan (HASP) shall be reviewed prior to DP-GSCP installation. All requirements of the HASP should be maintained for the duration of the installation. Any unforeseen hazards not specifically referenced in the HASP, identified by field personnel shall be reported to the Project Manager prior to proceeding with field activities.

3.1 Borehole Installation

DP drilling methods and borehole installation practices are discussed in *SOP No. 013 – Soil Boring Methods*. When a boring may be used for the construction of a DP-GSCP, the DP subcontractor should ensure that all down-hole equipment has been decontaminated in accordance with *SOP No. 016 Equipment Decontamination*. No grease or other machine lubricants should be used during the DP-GSCP installation.

3.2 Well Casing and Screen

The well casing (riser pipe) and screen for most DP-GSCPs will be between 0.5-foot and 2-inches in diameter. Threaded, schedule 40 PVC well casing and screens shall be used for DP-GSCP applications. The threaded joints may include an O-ring that, when properly installed, assures a leak-tight joint. Threaded joints also reduce the chance of introducing organic constituents to the well, which may occur when solvents are used to weld PVC pipe. The threaded joints also provide a smooth interior, which reduces the likelihood that sampling tools or measuring tapes will become hung up inside the well. Teflon® tape may be used to lubricate threads, and clean water or hydrated bentonite may be used to lubricate O-rings. Glued or solvent welded joints shall not be used for any DC-GSCP construction.

The well casing and screens should always be new material. Proper storage, both at the site and before delivery, is required to assure the pipe is clean.

A threaded, slip-over or an expanding-type well cap should top each DP-GSCP. A threaded plug should be installed in the bottom of the DP-GSCP.

3.3 Annulus Filling

Naturally developing a monitoring well (allowing the natural formation sands to cave around the well screen) is acceptable when the grain size distribution of the formation is known and the well screen was properly selected to retain the formation sand. However, this information is not usually available before the well is constructed. Consequently, most monitoring wells will be filter packed.

Filter pack sand should be clean, uniformly sized silica sand, free of organic matter and carbonate grains. The filter pack should be placed from the bottom of the well to no less than 1 foot nor more than 2 feet above the well screen. The filter pack should not be allowed to free fall through the water column, as this may cause the sand to segregate by grain size. The filter pack sand should be washed into place through a tremie pipe with water from a potable source; however, if the top of the PVC is set to a depth that is above the water table (i.e. within the unsaturated zone), the filter pack may be poured directly into the boring. A 0.5-foot thick of granular bentonite should be placed at the top of the filter pack and hydrated to separate the filter pack from the overlying bentonite seal.

A bentonite seal should be placed in the well above the filter pack sand. Bentonite pellets, chips or natural chunks may be used if they are hydrated with potable water during installation. The bentonite seal should extend from the top of the granular bentonite up the annular space to within 0.5 feet of the surface where a second 0.5-foot thick layer of granular bentonite should top the bentonite seal.

Prepacked well screens may be used. Pre-packed screens are generally composed of a rigid Type I PVC screen surrounded by a pre-sized filter pack. The filter pack is held in place by a stainless-steel wire mesh (for organic contaminants) or food-grade plastic mesh (for inorganic contaminants), such as polyethylene, that is anchored to the top and bottom of the screen. Sleeved screens consist of a stainless-steel wire mesh jacket filled with a pre-sized filter-pack material, which can be slipped over a PVC pipe base with slots of any size.

The specific construction method for each DP-GSCP sand pack (i.e. addition from the surface or pre-pack screens) will be discussed in the individual parcel work plan. The justification for the selected method will be provided in the text and applicable tables of the work plan, and will based on the available knowledge of the existing stratigraphy.

3.4 DP-GSCP Completion Log:

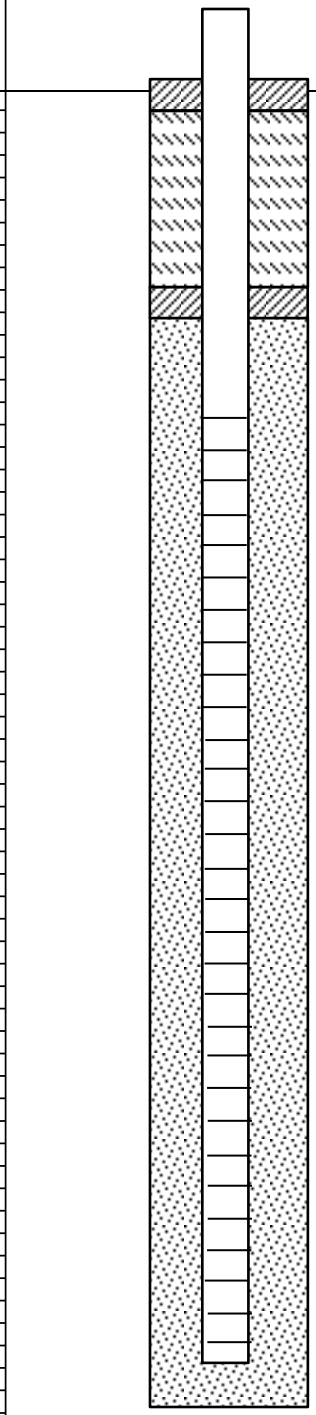
A soil boring log should be completed for each location as presented in *SOP No. 012 Geologic Logging*. A DP-GSCP completion log should also be completed and present, at a minimum the following:

- DP-GSCP name
- Name of individual logging the DP-GSCP
- Project specific information
- DP-GSCP survey coordinates
- 24-hour depth to water
- Completion Diagram
    - Detailed schematic which indicates but is not limited to:
        - Borehole diameter and depth
        - Diameter, and depth of DP-GSCP
        - Type and length of casing and screen
        - Slotted screen size
        - Grain size of sand pack
        - Depth to top of screen, sand pack and bentonite seal
        - Top of the well casing in mean sea level (MSL) elevation in feet. Elevation measurements should be determined by a Professional Land Surveyor following completion of the monitoring well.
        - Top of screen, bottom of screen, and bottom of well in feet below ground surface.

Temporary Groundwater Sample Point Construction Log

Sample Point ID:

Project Name: Project Number: Client: Site: Borehole Location: Sample Point Type:	Date/Time Started: Date/Time Completed: Logged by: Checked by: Driller:	Northing (ft): Easting (ft): Surface Elevation (ft), AMSL: Total Depth (ft): Depth to Water (ft): Borehole Diameter (in):

Depth (ft):	SAMPLE POINT CONSTRUCTION DIAGRAM	LITHOLOGIC DESCRIPTION	COMPLETION DETAILS
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15			Riser Type: Riser Diameter: _____ in. Riser Amount: _____ in. _____ lf Riser stickup (AGS): _____ in. Top of Riser Elev., ft (AMSL): _____ Screen Type: Screen Diameter: _____ in. Screen Amount: _____ in. _____ lf Slot Size: Bentonite Seal Granular Bentonite: top: bottom: Bentonite Chip: top: bottom: Granular Bentonite: top: bottom: Filter Pack: top: bottom: Grain size: Prepacked?: REMARKS:

APPENDIX B

Laboratory Standard Operating Procedures

Appendix B Table of Contents

STANDARD OPERATING PROCEDURE

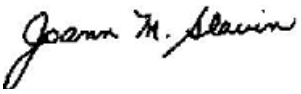
ANALYSIS OF VOLATILE ORGANICS IN AMBIENT AIR USING SUMMA OR OTHER SPECIALLY PREPARED CANISTERS BY GC/MS

PROJECT Specific Requirements for Sparrow Point Project

Reference Methods: EPA METHOD TO-15

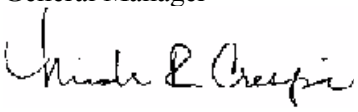
Local SOP Number:	S-LI-O-022-rev.01
Effective Date:	Date of Final Signature
Supersedes:	S-LI-O-022-rev.00

APPROVALS



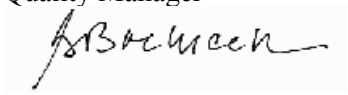
8/17/15

General Manager — Date



8/17/15

Quality Manager — Date



8/17/15

Department Manager — Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

TABLE OF CONTENTS

SECTION **PAGE**

1. **Identification of Test Method**

1.1. This Standard Operating Procedure (SOP) describes the procedure for the analysis of ambient air by Method TO-15 for the Sparrow Point Project.

2. **Summary of Method**

2.1. Sample collection is not performed by the laboratory, but collected samples are provided by the client.

2.2. The samples are collected in specially treated canisters.

2.3. Upon receipt at the laboratory, the canister tag data are recorded, the COC completed, pressures checked and recorded, and sample canisters stored until analysis.

2.4. For concentration o/f the analytes before analysis, the canister is attached to the sample preparation train.

2.5. In the preparation system, a predetermined volume of the air sample, measured with a mass flow controller, is collected on the multi-trap concentration unit.

2.6. Excessive water is handled with a ”Microscale Purge & Trap Water Management” in an Entech 7100 concentrator.

2.7. The temperature of the trap is raised and the analytes originally collected in the traps are desorbed and introduced into the GC.

2.8. The compounds are eluted from the capillary column with a temperature program to achieve separation.

2.9. The compounds are detected on an electron impact mass spectrometer and integrated on a data system, capable of collecting spectral data for identification and quantitation.

2.10. The mass spectrometer is operated in the Full Scan Mode., (SIM mode may be employed if necessary).

2.10.1. In Full Scan mode, the MS becomes a universal detector, often detecting compounds, which are not detected by the multi-detector approach.

2.10.2. The GC/MS/Scan is operated by continuously scanning a wide range of mass to charge ratios. Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound and will provide positive identification by means of spectra matching.

2.11. Targeted and “tentatively identified compounds” are evaluated and reported. Data packages are assembled, if full documentation is required.

3. **Scope and Application**

3.1. The protocol is applicable for analysis of low concentrations of volatile compounds in air.

3.2. The method involves whole air sampling with concentration of the analytes on a trap in the laboratory.

3.3. Generally, 0.6L to 6L canisters are used for sampling. Larger canisters can be used, if high sensitivity is desired, that requires a large volume for concentrating. Larger canisters also offer the advantage of having a larger sample volume available for re-analyses but have the drawback that they are harder to handle and clean.

3.4. Analysis according to method TO-15 is performed by GC/MS

3.5. Method TO-15 presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and sub-atmospheric pressure sampling).

3.6. The method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and sub-atmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters

3.7. Attachment I presents a list of the targeted analytes. Other analytes can be added, dependent on client needs.

3.8. Peaks for non-targeted compounds can be subjected to a computer search using the NIST library for tentative identification. The quantification of these “tentatively identified compounds” (TICs) is estimated, based on total area counts.

3.9. The procedure involves concentration of a sample volume on a trap. The sensitivity of the method will depend on the sample volume introduced into the instrument for concentration.

4. **Applicable Matrices**

4.1. The method is intended for analysis of volatile compounds in air.

5. **Limits of Detection and Quantitation**

5.1. The practical quantification limit (PQL) is the standard lab reporting limit. The Limit of Quantification (LOQ) represents the lowest value that can be reported without qualification (defined by the lowest calibration standard that can be verified with a certain level of accuracy). See Attachment I for PQL and LOQ.

5.2. Reporting limits must be determined at the start of a project and reporting conventions must be established with the client. Project specific requirements must be communicated to analysts prior to sample analysis.

5.3. MDL studies are performed annually by the analysis of seven low level standards at three to five times the expected MDL and calculated by the procedure defined in 40CFR Part 136 Appendix B.

5.4. The MDLs define the lowest levels, where positives will be found with 99 percent confidence with the particular analytical method in clean media.

5.5. Analyze the extracts on a calibrated instrument that meets all performance check criteria. Tabulate the results and statistically evaluate the standard deviations.

5.6. From the obtained standard deviation (S) calculate the MDL as follows:

Method Detection Limit (MDL)
MDL = tn-1 x S

Where:

S = Standard deviation
tn-1 = Students t-Test value (for seven replicates tn-1 = 3.14)

5.7. See Attachment I for MDLs. Current Method Detection Limits (MDLs) are on file and available by request from the Quality Manager.

6. **Interferences**

6.1. Interferences can be compounds contained in the sample, which are “interfering” with the analysis, or secondary contaminations from the instrument or compounds introduced during sample storage.

6.2. Interferences can be compounds contained in the sample, which are “interfering” with the analysis, or secondary contaminations from the instrument or compounds introduced during shipping or sample storage.

6.3. If other analytes are interfering, (co-eluting), identification of the targeted analytes is generally still possible, by comparison with the standard spectra. However, TICs cannot be identified, if co-eluting with each other or secondary contaminations.

6.4. Interferences can stem from the samples or may consist of secondary contamination that permeated into the canisters, primarily freons or solvent vapors present in the lab atmosphere.

6.5. Primarily canisters that were sampled at sub-atmospheric pressure are prone to secondary contamination. To avoid introduction of interferences, it is imperative that the canisters are stored in an environment free of contamination.

6.6. Other interferences may stem from the analytical instrument. Method blanks are required before samples are analyzed in each 24 h period to demonstrate that the instrument is free from contamination. Additional instrument blanks are introduced, if contamination of the instrument may have occurred.

6.7. After analyzing highly concentrated samples, blanks need to be interspersed to demonstrate that no contamination is carried over into the next run.

6.8. Late eluting compounds may interfere with the subsequent analysis. To elute higher boiling compounds from the column, hold the GC at least for 3 min. at the highest temperature of the program after the retention time of the last analyte**.**

7. Sample Collection, Preservation, Shipment and Storage

7.1. Sample Collection

7.1.1. Sample collection is not performed by the laboratory. Canisters and cleaning certification are provided.

7.2. The holding time for canisters in the field from the time the canisters leave the laboratory until collection is 15 days, to assure that adequate vacuum is maintained.

7.2.1. Project specific holding times from 10 days sample receipt to lab and 14 days from collection.

7.3. Detailed information about sampling apparatus, sampling train setup, flow-rate adjustments, ambient requirements, cleaning procedure for the sampling train, and recording requirements are to be checked in method TO-15.

7.4. Sampling procedures will vary depending on whether sub-atmospheric pressure or pressurized sampling mode is employed. For sub-atmospheric pressure, proceed as follows.

7.4.1. Evacuated canisters are opened to the atmosphere containing the VOCs to be sampled. The differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted average (TWA) samples (duration of 1-24 hours) taken through a flow restrictive inlet (e.g., mass flow controller, critical orifice).

7.4.2. For grab samples critical orifices or constant pressure differential critical orifices are used. With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller or pressure regulated critical orifice, the sub-atmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

7.4.3. All pertinent data for the sampling site, e.g. ambient conditions, as well as the parameters for the individual samples have to be recorded in Field Test Data Sheets (FTDS)

7.5. Sample Preservation and Handling

7.5.1. For transport to and from the site, the canisters have to be packaged to protect the valve. There is no temperature requirement during transfer and storage in the laboratory.

7.5.2. Samples in stainless steel canisters must be analyzed within 30 days from sample collection.

8. **Cleaning of Canisters, Clean Canister Certification and Leak Checking and**

8.1. Cleaning of Canisters

8.1.1. A canister cleaning system is assembled with a vacuum pump hooked up to a manifold for the canisters**.**

8.1.2. The cleaning procedure is programmed into the cleaning instrument, and the entire cleaning procedure, temperatures, cycles and pressures are recorded in the Canister Log.

8.1.3. Additionally, the serial numbers of the canisters and cleaning process is recorded in the LIMS. Canisters are tracked, and therefore the cleaning can be matched with the shipping records and the analytical data for the samples that were sampled in the canister previously.

8.1.4. The vent shut-off valve and the canister valves are opened to release any remaining pressure in the canisters. They are then connected to the cleaning manifold and are placed in a conditioning oven and may be heated not to exceed 100°C.

8.1.5. The vacuum pump is started, the canister(s) are evacuated to <0.05mm Hg for at least one hour then pressurized to 30 psig for 3 or more cycles. According to EPA TO-15 Appendix B –"If canisters can be routinely certified while using higher" (actually higher pressure) "vacuum, then this criteria can be relaxed. However the ultimate vacuum achieved during cleaning should always be < 0.2 mm Hg"

8.1.6. At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air followed by batch certification and leak check testing (as described in the following sections).

8.1.7. The canister valve is closed, the canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting.

8.2. Clean Canister Certification

8.2.1. After the cleaning process, the canister(s) is(are) then analyzed by a GC/MS analytical system.

8.2.2. Initially, 100 % of the canisters have to be analyzed,

8.2.3. After the cleanup system and canisters are proven reliable, one canister per cleaning batch has to be tested. A batch is defined as the number of canisters that are cleaned under the same conditions (temperature, time, cycles, and pressure). A maximum of 24 canisters may be cleaned in a single batch depending on canister size.

8.2.4. At the end of the evacuation/pressurization cycle, the canisters to be tested are pressurized to 206 kPa (30 psig) with humid zero air

8.2.5. These canisters are analyzed by a GC/MS. Any canister that shows targeted analytes above 0.2 ppbv cannot be used, and has to be re-cleaned.

8.2.6. Any canisters that contained samples with high concentrations should be checked after the cleaning process.

8.2.7. Cleaning procedures performed on the canisters and results of the cleaning check have to be recorded in the LIMS.

8.2.8. The analyst responsible for the preparation of the canisters and reads and records the final pressure of the canisters at the gauges before the canisters are shipped.

8.3. Leak Check of Canisters

8.3.1. All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air or nitrogen.

8.3.2. The initial pressure is measured, the canister value is closed, and the final pressure is checked after 24 hours. If leak tight, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.3.3. The leak check must be documented in the Canister Cleaning Log. Access the electronic logbook through the LIMS. Record the initial pressure and final pressure after the 24 hour period. If the pressure varies more than 2 psig, the problem must be investigated and resolved.

8.4. Once the cleaning process is complete, the certification canister has been proven to be clean and all cans are proven to be leak free, the "batch" of canisters are re-evacuated to -30 psig and are ready for shipment.

8.5. An identification tag is attached to each canister for field notes and chain-of-custody purposes.

9. **Definitions**

9.1. Definitions are described in the Pace Analytical Services Quality Manual.

9.2. Additional definitions related to this SOP are:

9.2.1. **Absolute Pressure—**pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.
9.2.2. **Clean canister certification batch:** A batch is defined as the number of canisters that are cleaned under the same conditions (temperature, time, cycles, and pressure). A maximum of 24 canisters may be cleaned in a single batch depending on canister size
9.2.3. **Cryogen—**a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on frontof the analytical column. Typical cryogens are liquid nitrogen (bp -195.8EC), liquid argon (bp -185.7EC), and liquid CO (bp -79.5EC).
9.2.4. **Dynamic Calibration: —**calibration of an analytical system using calibration gas standard concentrationsin a form identical or very similar to the samples to be analyzed and by introducing such standards into the inletof the sampling or analytical system from a manifold through which the gas standards are flowing.
9.2.5. **Dynamic Dilution:—**means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

9.2.6. **Gauge Pressure**: —pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.
9.2.7. **Ms-Scan—**mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.
9.2.8. **Ms-Sim—**mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

10. **Equipment and Supplies**

10.1. Equipment and Supplies for Sample Collection

10.1.1. Specially treated stainless steel canisters, of a volume of 0.6 L, 1 L, 2.7 L, 3.2 L, or 6L. All sizes are suitable for soil gas and 6 L to be used for indoor air and ambient samples.

10.1.2. Canisters are certified clean (<0.2 ppbv of targeted VOCs according to the cleaning procedure in Section 7.7)

10.1.3. Each canister has to be equipped with a flow controller (unless grab samples are taken), pressure gauge, critical orifice, and stainless steel frit dust filter over the orifice. The flow controller may be preset by the laboratory, unless grab samples are taken.

10.1.4. The canisters must be equipped with sample inlets or sampling caps (to prevent water droplets to accumulate that could enter the sampling train) as well as a hard seat metal valve for shutoff.

10.1.5. Interior surfaces of canisters are treated by any of a number of passivation processes, one of which is SUMMA polishing as identified in the original Compendium Method TO-14. Other specially prepared canisters are also available from various manufacturers:

- BRC/Ramussen 17010 NW Skyline Blvd. Portland, OR 97321
- Meriter 1790 Potrero Drive San Jose, CA 95124
- Restec Corporation 110 Benner Circle Bellefonte, PA 16823-8812
- XonTech Inc. 6862 Hayenhurst Avenue Van Nuys, CA 91406
- Scientific Instrumentation Specialists P.O. Box 8941 Moscow, ID 83843
- Graseby 500 Technology Ct. Smyrna, GA 30832
- Entech Instruments, Inc. 2207 Agate Court, Simi Valley, CA 93065

10.1.6. For cleaning before shipping canister to client for sampling, the canister is evacuated to <0.05 mm of mercury.

- Electronic Mass Flow Controllers (3). Maintain constant flow (for carrier gas and sample gas) and to provide analog output to monitor flow anomalies, Tylan Model 260, 0–100 mL/min, or equivalent. (A model with a flow rate up to 200 mL may be used in particular for 6 L samples.)

- The flow controller is preset at a flow rate suitable for collection: (At 100 mL /min) and an orifice of 0.006 inches a 6L canister will fill in 1 h and a 2.5 or 3.2 L canister in about 30 min.) Interior samples should be collected over 8-24 h at the appropriate flow controller setting.

10.2. Equipment and Supplies for Sample Preparation

10.2.1. Vacuum Pumps (Oil less rough pump / Molecular drag). Capable of evacuating sample canister(s) to an absolute pressure of <0.05 mm Hg.

10.2.2. Manifold. Fused silica coated stainless steel manifold with connections for simultaneously cleaning several canisters in an elevated temperature controlled oven. (Entech 3100A Canister Cleaner or equiv.)

10.2.3. Vacuum Gauge. Capable of measuring vacuum in the manifold to an absolute pressure of 0.05 mm Hg or less.

10.2.4. Stainless Steel Pressure Gauges (2). (–30-0-30psig) to monitor pressure.

10.2.5. Stainless Steel Flow Control Valve. To regulate flow of zero air into canister(s).

10.2.6. Gas Cylinders of Zero Air. Ultrahigh purity grade.

10.2.7. Humidifier -, pressurizable water bubbler, containing HPLC-grade deionized water, with Swagelok connections to fit calibration gas preparation train and canister cleaning manifold.

10.2.8. Vacuum Pump. General purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap, Thomas Industries, Inc., Sheboygan, WI, Model 107BA20, or equivalent.

10.2.9. Chromatographic Grade Stainless Steel Tubing and Stainless Steel Plumbing Fittings.

10.2.10. Oven - capable of maintaining 105°C.

10.2.11. Sample concentrator such as the Entech 7100A or equivalent, Entech 7032 auto.

10.2.12. Sampler, used for sequential sample preparation steps, interfaced with the GC/MS.

10.2.13. Entech 4600A dynamic diluter.

10.2.14. Entech 3100A canister cleaner module.

10.3. Equipment and Supplies for Instrument Analysis

10.3.1. Humidifier -, pressurizable water bubbler, containing HPLC-grade deionized water, with Swagelok connections to fit calibration gas preparation train and canister cleaning manifold.

10.3.2. Liquid nitrogen

10.3.3. Gas Chromatograph - with programmable temperature control, carrier gas control.

10.3.4. Capillary column - fused silica 60 m x 0.32 mm, 1.0 micron film thickness, RTX-1 from Restek or equivalent

10.3.5. Quadropole mass spectrometer - benchtop, with electron impact ionization and electron multiplier, scanning from 35 to 300 amu

10.3.6. Data system

- Computer
- Graphics display terminal
- Printer
- Chemstation/Enviroquant software from HP,
- Omega from Khemia, or equivalent
- Mass Spectral library - NIST 08.L

11. **Reagents and Standards**

11.1. **Table 11.1 – Reagents and Stock Standards-Sample Preparation**

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Organic-free Water (OFW)	De-ionized water	Verify that background levels of volatile compounds are acceptable by analysis
Gas cylinders of helium	Ultrahigh purity grade	
Gas cylinders of nitrogen	Ultrahigh purity grade	
Gas cylinders of zero air	Ultrahigh purity grade	
Internal standard stock	Neat Standards or Gas Cylinder with Internal Standards and BFB: Bromochloromethane (IS),1,4-difluorobenzene (IS),chlorobenzene-d5 (IS), bromofluorobenzene at 1000 ppbv	
Internal standard working	Canister with working standard mix for calibration containing all targeted analytes prepared from certified calibration mix with manifold at 50 ppbv (Only 100 mL are injected of the IS gas to achieve the equivalent of 10 ppbv for 500 mL injection)	
Cryogen, liquid nitrogen (bp – 195.8EC)		
Cryogen -liquid argon (bp – 185.7EC		

11.2. **Table 11.2 – Reagents and Stock Standards-Instrument Analysis**

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Perfluoro-tri-N-butylamine (PFTBA)	Tuning compound	
Instrument Performance Check Gas Standard - Bromofluorobenzene (BFB)	Performance Check Standard at 50 ng/injection	BFB cannot be combined with the calibration standard. BFB is contained in the internal standard mix, which can be used.
Calibration gas stock	Certified Gas Cylinder with Calibrated Gas Standard Mix for all targeted analytes at a concentration of 1000 ppbv	Spectra Gases & Air Liquide / Scott. Traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM)
Calibration gas working standard	0.2-40 ppbv all targeted analytes	Canister prepared from stock
Calibration Verification gas stock	Certified Gas Cylinder with Calibrated Gas Standard Mix for all targeted analytes at a concentration of 1000 ppbv	Restek -Traceable to a National Institute of Standards and Technology (NIST)Standard Reference Material (SRM)
Calibration Verification gas stock working	10 ppbv all targeted analytes	

11.3. Standard Preparation by Dynamic Dilution Technique

11.4. Standards are prepared by dynamic dilution of cylinder(s) containing gas calibration stock standards with humidified zero air using mass flow controllers and a manifold. The working standard may be delivered from the manifold to a clean evacuated canister using mass flow controllers. For example, a calibration standard at 20ppbv is prepared by diluting a 1000 ppbv stock standard 50x. This is accomplished by dynamically diluting, or mixing, two mass flow controlled gas streams of 980 ml/min diluent gas and 20 ml/min 1000 ppbv stock standard mix. The mass flow controllers used for this process are software controlled. These working standards are then analyzed..

11.5. Holding Times of Standards

11.5.1. The certified NIST stock standards can be held for one year or according to manufacturer recommendation.

11.5.2. Working standards prepared in canisters may be stored for thirty days (or less if working standards are no longer viable) in an atmosphere free of potential contaminants.

11.6. Standard Logs

11.6.1. Record all standards in the log book.

11.6.2. Certifications and Copies of the Certificates of Analysis from the supplier for each lot must be filed.

12. **Calibration and Standardization**

12.1. Tuning and Performance Check

12.1.1. After major changes of parameters or instrument maintenance that affects the source of the MS, the source has to be tuned. Adjust all voltages; obtain ion ratios for the tuning compound PFTBA, as established for the specific instrument, to achieve the required BFB ion ratios

12.1.2. Before running calibrations or analyses, check the correct mass calibration with the analysis of 50 ng of the performance check compound BFB. Optionally, the internal standard gas mix can be used. BFB analysis is required one every 24 hours and before any standards or samples are analyzed.

12.1.3. Three scans (peaks apex scan and scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan no more than 20 scans prior to BFB elution

12.1.4. Compare ion ratios found against the EPA acceptance criteria, which are listed in Attachment V. If the abundances do not meet the criteria, retune or adjust voltages based on experience before repeating the BFB check

12.1.5. Documentation of acceptable mass calibration must be provided by the mass listing and bar graph plot for the BFB spectrum.

12.2. Initial Calibration

12.2.1. In the calibration, the relative response is determined for the major ion of each analyte relative to the major ion of an internal standard. The primary and secondary ions of the analytes are listed in Attachment III.

12.2.2. A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. Standards for the multipoint calibration are analyzed from the reporting limit 0.2 ppbv to 40 ppbv. For specific projects lower calibration levels of 0.025 and 0.1 ppbv are included. The curve fit must be linear.

12.2.3. Preparation of Working Standard Canisters

- Assemble the standard preparation train
- Attach a certified clean canister via flow-controller to a two–way valve that is attached to the calibration gas and a tank with zero air in line with a humidifier.
- With the dynamic mixing device adjust flows of the Standard gas mixture and zero air or nitrogen to yield a mixture at the desired concentration.
- This mixture is filled into an empty, clean canister.

12.2.4. Generally only one canister is prepared. Two or more different working calibration canisters may be prepared to cover the entire calibration range.

12.2.5. The working calibration gas canister is connected to the sample preparation train in lieu of a sample canister. The volume of the calibration gas is determined by the time setting and flow rate,

checked with the flow-controller. The volume is varied for multipoint calibration at different levels between 20 to 400 mL.

12.2.6. It has been found that for these volumes no differences for the calibrations are observed even without adding any make-up gas. Linearity is achieved even without make-up gas.

12.2.7. In the calibration, the relative response is determined for the major ion each analyte relative to the major ion of an internal standard. The primary and secondary ions of the analytes are listed in Attachment III. The calibration is performed using different volumes of the calibration gas mix.

12.2.8. Perform a multipoint calibration with a minimum of five to establish linearity for all targeted analytes compounds between reporting limits and the highest calibration level that can conveniently be achieved with the calibration gas.

12.2.9. Since relative responses by internal standard method are to be determined, each calibration mix must also be spiked with the internal standards.

12.2.10. Equally, all samples are to be spiked with internal standards.

12.2.11. Calculate relative response factors for all analytes utilizing the appropriate internal standard.

12.2.12. Compute the responses with the following formula:

Relative Response Factor (RRF)

$$RRF = \frac{A_x \times IS}{A_{is} \times Amount_x} \frac{\sqrt{\sum (RF_i - RF_{avg})^2/(n-1)}}{RF_{avg}} \times 100\%$$

Where:
Ax = Area of characteristic ion for compound measured
IS = Amount of internal standard
Ais = Area of the characteristic ion for the specific internal standard
$Amount_x$ = Amount of compound to be measured

12.2.13. Determine the average response factor by summing factors of all concentration levels and dividing the sum by the number of results.

12.2.14. Evaluate the multipoint calibration for relative standard deviation with the following computation:

Relative Standard Deviation (RSD)%

$$RSD = \frac{\sqrt{\sum (RF_i - RF_{avg})^2/(n-1)}}{RF_{avg}} \times 100\%$$

Where:
RFi = Response factor from the ith calibration run
RF avg = Average response factor for the analyte
n = Number of calibration points for the analyte

12.2.15. The relative standard deviation (RSD) of the response factors should be <30% for the curve to be acceptable. Two RSDs may exceed 30 %, but must be under 40 %.

12.2.16. If a particular analysis appears to be an outlier, re-analyze that level.

12.2.17. If the criteria still cannot be met, determine the cause and take remedial action in regard to instrument maintenance or replacement of standard solutions, then perform a new multipoint calibration.

12.2.18. The samples are calculated using the mean of the response factors.

12.2.19. The Relative Retention Times (RRT) for all targeted compounds should also be calculated.

12.2.20. The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound.

12.2.21. The Primary Ion Area Response (Y) for Internal Standards should be tabulated and the mean of these areas should be calculated.

12.2.22. The area response Y for each initial calibration level must be within 40% of the mean response for that analyte in that calibration.

12.2.23. The Mean Retention Time (RT) of each internal standard in the initial calibration should be calculated

12.2.24. The retention time shift of each internal standard at each level must be within 20 s of the mean retention for that internal standard in the initial calibration.

12.3. Initial Calibration Verification (ICV)

12.3.1. Immediately following every initial calibration, calibration verification with a standard of a different source must be analyzed.

12.3.2. The ICV is analyzed at the same level as the CCV, discussed below, and should meet the same acceptance criteria.

12.4. Verification of Mass Calibration

12.4.1. On a daily basis before continuous calibration verification, check that the tune parameters with the analysis of 50 ng of the performance check substance BFB.

12.4.2. Check that the obtained ratios meet the acceptance criteria of Attachment V. If the ion ratios are outside the limits, adjust the tune parameters until satisfactory ratios are obtained.

12.5. Continuous Calibration Verification (CCV)

12.5.1. Ongoing analyses of standards on a daily basis are for verification only. All quantifications are performed with the factors of the initial calibration.

12.5.2. Once correct tuning is verified, instrument calibration for relative response factors is checked with an injection of a calibration standard containing a mid-level or 10 ppbv of each analyte and internal standard.

12.5.3. Calculate the RRF and compute the relative percent difference with the following equation:

Percent Difference (% D)

$$\% D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} \times 100\%$$

Where:
RRF_{avg} = Average RRF of initial calibration
RRF_c = RRF of continuous calibration

12.5.4. %D for each analyte must be within ± 30% for the calibration verification (CCV) for continued use of the average response factor from the initial calibration.

12.5.5. If the results are acceptable, proceed with the analyses. Otherwise repeat the analysis, either with a different continuous calibration standard, if a problem with the solution is suspected, or after minor remedial action is performed.

12.5.6. If acceptance criteria cannot be achieved, a new multipoint calibration needs to be analyzed.

12.6. Internal Standard Area Checks

12.6.1. To assure stability of instrument performance and injections, the internal standard (IS) areas of all injections are monitored.

12.6.2. Tabulate all IS areas for a 24 hour period starting with the continuous calibration.

12.6.3. Compare areas and retention times with those of the continuous calibration (or medium level standard in a multipoint calibration). Areas should be between ±40 percent, and retention times within 0.33 minutes.

12.7. Analytical Sequence

12.7.1. The analytical sequence includes the following analyses:

- Tuning with BFB
- Continuous Calibration Check (CCV) unless an initial calibration is performed
- Method Blank

- Lab Fortified Blank ("Audit Sample")
- Samples
- Sample Duplicate, if sample volume allows

13. **Procedure**

13.1. Instrument Setup

13.1.1. Typical operating parameters of the analytical system are presented in Attachment II.

13.1.2. Carrier flow velocities and temperature programs depend on the individual column used and have to be optimized for the specific column. Equally, the parameters for the mass spectrometer have to be adjusted depending on the particular conditions

13.1.3. Set up instrument with the optimal operating parameters and the data system with the appropriate Scan acquisition / processing method. (Consult instrument operating procedures and manual for the data system.)

13.1.4. Enter a sequence into the data system reflecting the sequence in which the canisters are to be analyzed

13.1.5. Before samples are loaded on the instrument, the levels of the samples and reporting limits should be investigated from precedence data or information from the client to determine the volume of sample to be entered into the instrument.

13.1.6. If no information about the sample level is available, the samples may have to be prescreened as discussed under sample analysis.

13.1.7. The canister is connected via a flow-controller to the concentration train. (Entech 7032 / Entech 7100)

13.1.8. In sequential order, as entered in the "sequence", specified under "analysis", the calibration canister, blank canister and sample canisters are connected to the auto-sampler, Entech 7032, which is connected to the concentrator Entech 7100.

13.1.9. Set the flow-controller and timing device to the calculated values to supply the desired sample volumes. As for the calibrations, a total injection volume of 400 mL is introduced into the system. Depending on the sample volume that can range from 20 mL to 400 mL, the appropriate amount of make-up gas of humidified zero air should be added by the system.

13.1.10. Alternatively sampling loops of different sizes can be used for small sample volumes

13.1.11. In addition, splitting is another option for high sample concentrations.

13.1.12. Upon opening of the valve of the canister, the appropriate amount of sample is transferred to the trap of the Concentrator unit. The volume of sample is determined by the appropriate setting of the time and flow-rate during the adsorption process

13.1.13. Each sample is "spiked" during this process with internal standard compounds by sampling an additional 80 mL of the internal standard working gas mixture onto the concentrating trap.

13.2. Sample Analysis

13.2.1. Prescreening of Samples

- Unless previous knowledge of sample concentration exists, all samples should be analyzed at a small volume, e. g. 20 mL, to guard against contamination of the instrument.
- Based on the results, an appropriate sample volume is then used for analysis.

13.2.2. Three Stage Concentration of Sample on Instrument

- Typically 400 mL of sample is trapped cryogenically on glass bead traps at -150°C
- The glass bead trap is desorbed at 10°C to a Tenax trap at -30°C
- The Tenax trap is back flushed at 180°C at 180°C and focused at -160°C in a focusing trap

13.2.3. Analysis

- The compounds are desorbed from the focusing trap at elevated temperature onto the analytical column.
- The compounds are eluted from the column with a temperature program to achieve separation.
- The eluting compounds are detected on an electron impact mass spectrometer and collected on the data system with the Chemstation software and processed with either the Enviroquant, or Omega by Khemia.

14. **Quality Control**

14.1. The sample preparation efficiency is continuously checked by spiking all samples with surrogate compounds and analyzing quality control samples on an ongoing basis. Minimum detection limits (MDL) for the method are checked on a yearly basis.

14.2. Accuracy, Lab fortified blanks (LFB)

14.2.1. Accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\% \text{ Accuracy} = (\text{Spiked Value} - \text{Observed Value} / \text{Spiked Value}) \times 100$$

14.2.2. Analyze a control sample (LFB) at 10 ppbv, using the calibration verification gas mix. Acceptance limit for Accuracy is 70-130 %. The frequency of LFB analysis is once per 24 hr tune period.

14.3. Precision of Duplicates

14.3.1. Precision of the methodology is checked by analyzing sample duplicates. Method TO-15 does not specify the frequency for sample duplicates. As possible, one duplicate should be analyzed with each batch of samples. Duplicates are to be analyzed one per batch of 20 samples.

14.3.2. If duplicate samples were analyzed, calculate the relative percent difference as follows.

$$\%RPD = \frac{X1 - X2}{X} * 100$$

Where:

%RPD= Relative Percent Difference
X1 = Measurement taken for volume 1
X2 = Measurement taken for volume 2
X = Average of the two values

14.3.3. Acceptance limit for %RPD is 25 %.

14.4. Method Blank

14.4.1. A method blank is analyzed for each 24 hours of analysis

14.4.2. The method blank must be analyzed immediately following the standard to ensure that there is no carryover.

14.4.3. The method blanks are analyzed with humidified ultra-pure zero air in dedicated certified canister that have not left the laboratory.

14.4.4. The internal standard areas must be within ±40% of the mean area response of the IS in the most recent calibration or verification.

14.4.5. Any interferences seen in the method blank must be less than reporting limit (PQL). If exception have to be made, in particular for acetone and methylene chloride.

14.4.6. If a method blank exceeds the above criteria, the source of the contamination must be found, and the problem eliminated prior to continuing with analysis.

14.4.7. If a sample exceeds the linear range of the calibration a blank is run immediately after the sample to determine if there is carry over. If a sample is run on the auto-sampler after a sample that exceeds the linear range, the sample is evaluated for carry over and reanalyzed if necessary.

15. **Data Analysis and Calculations**

15.1. Identification of Targeted Analytes

15.1.1. Compound identification is performed by "reverse library search" based on the computer algorithms for matching of the sample spectra with the library spectra developed in-house from standard injections.

15.1.2. All ions in the standard mass spectrum of a relative intensity greater than 10 percent of the most abundant ion must be present, and the relative intensities of the ions must agree within ± 30 percent. The ions greater than 10 percent in the sample but not in the standard spectrum must be accounted for.

15.1.3. Another means of identifying compounds is by comparison of the relative retention time of the sample peak with that in the standard analysis. The relative retention times (RRT) should not deviate by more than ± 0.06 RRT units. This serves as a confirmation of the spectra identification and provides a means to distinguish compounds with the same spectra but with different elution times.

15.2. Tentatively Identified Compounds (TICs)

15.2.1. In the retention time window from 30 sec before the earliest targeted analyte and 3 min. after the latest targeted analyte select the largest 20 peaks that are neither identified as spiked compounds nor as targeted analytes. Total areas of the peaks have to be larger than 10 % of the closest internal standard.

15.2.2. "Tentatively identify" the selected peaks by performing a forward library search, to match their spectra to those in the NIST/EPA/MSDC library.

15.2.3. The algorithms for the match "best fit" are based upon US EPA criteria:

- The major ions in the reference spectra, greater than 10 percent of the most abundant ion, should be present.
- The molecular ions in the reference spectrum (if present) must also be found in the sample spectrum.

15.2.4. Review the ions in the sample spectrum that are not part of the reference spectrum for interference. Ions, contributed by background and unresolved compounds, can be subtracted by the computer software.

15.2.5. If no good match can be found that satisfies the above criteria, report the analyte as an unknown compound, but if possible, categorize the type of analyte, e.g. as aromatic, alcohol, etc.

15.2.6. If spectra are encountered that contain the typical ions of the breakdown products of the liquid phase of the analytical column (methyl siloxanes), qualify the compounds as "suspected column bleed".

15.3. Quantification of Targeted Analytes

15.3.1. If the computer search establishes a positive, the concentration of the analyte is computed by the software program with the RRFs of the calibration established by internal standard method and reported in the "quant report".

15.3.2. The RRF used is either from the mid-level of the multipoint calibration for those samples analyzed subsequently, or the daily RRF of the continuous calibration for samples analyzed on other days.

15.3.3. The data system is capable of computing the reportable sample concentration, if the appropriate parameters are entered according to the following computation:

$$\text{Conc} = \frac{A_x \times IS}{A_{is} \times RRF_o}$$

Where:

Conc = Concentration of analyte in air collected in ppbv
Ax = Area of characteristic ion of analyte
Ais = Area of characteristic ion of internal standard
IS = Amount of internal standard
RRF = Relative response factor of analyte

15.3.4. The total xylene is reported for the summed area of the two peaks utilizing the response factor o-xylene.

15.3.5. For conversion from ppbv into µg/m_3, the following equation is used.

$$\text{Conc (ppb v/v)} = \text{Conc } (\mu g/m^3) \times CV$$

Where:

$$CV = \frac{24.45}{MW}$$

For routine computations, conversion factors (CV) can be calculated and stored:

15.4. Quantification of TICs

15.4.1. The calculation for concentration is performed with the same formula as above, however, since no calibration factors are available, a response factor of one is assumed.

15.4.2. Unlikely in the case of the targeted analytes, the total area for all ions is determined, and likewise, the total area for the associated internal standard is used in the computation.

15.4.3. The resulting quantity represents an estimated value and therefore has to be flagged with the qualifier "J".

15.4.4. Conversion of TIC concentration from ppbv into µg/m^3 can only be performed if the analyte was identified and the MW is known.

15.5. Dilution of Samples

15.5.1. If the concentration of any targeted analytes in the sample exceeds the calibration range, the sample has to be reanalyzed at a dilution.

15.5.2. In order to "dilute" the sample, an appropriately smaller volume of the sample has to be injected. This, however, is limited to injection volumes down to 20 mL, which achieves a dilution of 1:20.

15.5.3. For any larger dilutions, dilutions in canisters are prepared by mixing aliquots of the sample with humidified zero air, using the automated mixing device of the Entech instrument.

16. **Data Assessment and Acceptance Criteria for Quality Control Measures**

16.1. The analyst is responsible for generating the data and also is the initial individual to review the data. The review must include at least the following procedures (where applicable):

16.1.1. Inspection of records in run log for completeness;

- Standard and reagent lot numbers, support equipment, spike amounts, calculations, dilution factors, container/bottle used for analysis, reporting limits.

16.1.2. Determination of whether the results meet the laboratory-specific quality control criteria;

16.1.3. Checks to determine consistency with client/project-specific measurement quality objectives (MQOs) if such exists;

16.1.4. Checks to ensure that the appropriate sample preparatory and analytical SOPs and methods were followed, and that chain-of-custody and holding time requirements were met;

16.1.5. Checks to ensure that all calibration and quality control requirements were met;

16.1.6. Checks for complete and accurate explanations of anomalous results, corrective action, and the use of data qualifiers in the case narrative or LIMS QC notes.

16.1.7. Record of any non-standard condition of the test, test environment, sample or any deviation from standard operating procedure.

16.2. If analysis is deemed acceptable, data will be imported into the LIMS.

16.2.1. Another review is performed for correctness of results, including prep factors, dilution factors, spike amounts and recoveries, sample and QC references and appropriate qualifiers.

16.2.2. If additional information is to be communicated to the data user about a particular sample, a “QC Note” is entered by the analyst.

16.2.3. Once data has been reviewed in the LIMS, the analyst or supervisor will “QA” the sequence which indicates the data has been reviewed and is ready for reporting.

16.3. Refer to Attachment VII for data assessment and acceptance criteria for quality control measures.

16.4. Once it has been established that the quality objectives are met, the finalized data are entered into the LIMS and may be reported.

17. Corrective Actions for Out-of-Control Data

17.1. Corrective action begins with the analysts who are responsible for knowing when the analytical process is out of control.

17.2. Corrective actions should be initiated for out of control events such as when QC checks exceed acceptance limits or exhibit trending, holding time failures, loss of sample, equipment malfunctions or evidence of sample contamination.

17.3. Refer to Tables Attachment VII for data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1. Refer to Attachment VII for data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

18.2. All problems associated with the analysis of a sample group should be outlined in the case narrative of the data package or with the use of QC Notes in the LIMS, if required.

19. Method Performance

19.1. The suitability of the method for the analytes tested was determined when the method was developed. During "method startup" in the laboratory, the capability of the analysts, suitability of equipment, materials and instrumentation was tested.

19.2. Internal method performance is established and monitored with use of the following (where applicable):

19.2.1. Method Detection Limit studies

19.2.2. Demonstration of Capability

- Every analyst who performs this method must first document acceptable accuracy and precision by passing an initial demonstration of capability study (IDC). See Attachment VII

19.2.3. Precision and accuracy

19.2.4. Positive and negative controls

19.2.5. Control Charts

19.2.6. Measurement of sample matrix effects

19.2.7. Quality Control Samples (Proficiency Testing)

20. Instrument/Equipment Maintenance/Troubleshooting

20.1. For information and guidance related to instrument/equipment maintenance, troubleshooting and computer hardware and software refer to the following documents:

Document # (latest revision)	Document Title
QAM	*Quality Assurance Quality Control Manual*
ADMIN002	*Computers and Programs*
MS045	*ENTECH 7100A Preconcentrator Operators Manual*
MS069	*ENTECH Tutorials (8 manuals)*
MS070	*"Canister Sampling and Analysis of VOC's in Air" ENTECH Air Academy PowerPoint*

20.2. Troubleshooting procedures also come from experience and training. Problems that the analyst encounters may be elevated to the department supervisor. Other means of problem resolution may come from review of prior related corrective action reports, instrument maintenance records, internal and external audits and lab notes.

21. **Safety**

21.1. All in-house safety regulations have to be observed during sample preparation and analysis.

21.1.1. Consult material handed out during orientation for handling of corrosives, flammable and toxic materials.

21.1.2. Use common sense and specially regard safety of coworkers.

21.2. Observe safety rules for working with chemicals in posted Code of Federal Regulations Section 29, Part 1910.1450.

21.3. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest level possible.

21.3.1. Read properties of chemical listed on label.

21.3.2. The reference file of material safety data sheets (MSDS) should be consulted for properties of the chemicals used, to determine handling precautions.

22. **Waste Management**

22.1. All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste.

22.2. Refer to the lab's *Sample and Waste Management* SOP.

23. **Pollution Prevention**

23.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Use pollution prevention techniques in laboratory operation whenever feasible.

23.2. Quantity of chemicals purchased should be based on expected usage during its shelf life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

23.3. Control releases from hood and bench operations and comply with discharge permits and regulations, hazardous waste identification rules, and land disposal restrictions.

23.4. The generated waste has to be disposed in a manner not to cause pollution.

23.5. All wastes deemed toxic are collected in the laboratory and are disposed by professional companies licensed in waste disposal.

23.6. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

24. **References**

23.7. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition* (EPA/625/R-96/010b). Method TO-15.

23.8. "New York State Department of Environmental Protection Analytical Services Protocol," June 2000

23.9. "New York State Department of Environmental Protection Analytical Services Protocol," April 2005

23.10. National Environmental Laboratory Accreditation Conference (NELAC) Constitution, Bylaws and Standard, approved June 5, 2003, (EPA/600/R-04/003)

23.11. 40CFR Part 136 Appendix B

23.12. 2009 TNI Laboratory Accreditation Standards, EL-V1-2009.

25. **Tables and Figures**

24.1. ATTACHMENT I: PRACTICAL QUANTIFICATION LIMITS (PQL), LIMIT OF QUANTITATION (LOQ) AND METHOD DETECTION LIMITS (MDL) FOR TARGETED VOLATILE ORGANICS

24.2. ATTACHMENT II: EXAMPLE OF INSTRUMENT OPERATING PARAMETERS FOR TO-15 ANALYSIS

24.3. ATTACHMENT III: CHARACTERISTIC IONS FOR VOLATILE TARGETED COMPOUNDS

24.4. ATTACHMENT IV: CHARACTERISTIC IONS FOR INTERNAL STANDARDS

24.5. ATTACHMENT V: BFB KEY IONS AND ION ABUNDANCE CRITERIA

24.6. ATTACHMENT VI: SYSTEM MONITORING COMPOUND RECOVERY LIMITS

24.7. ATTACHMENT VII: QUALITY CONTROL ACCEPTANCE CRITERIA AND CORRECTIVE ACTION PLAN

26. **Revisions**

Document Number	Reason for Change	Date
S-LI-O-022-rev.00	Created for Sparrow Point Project. Added µg/m³ PQL, MDL, edited compound list in Attachment I and III, holding time requirements, minimum 5 level calibration and added clarification to frequency of tune, LCS and DUP. Clarified Section 11.4 – standard preparation.	7/8/15
S-LI-O-022-rev.01	Modified Section 12.2.2 to read "A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. Standards for the multipoint calibration are analyzed from the reporting limit 0.2 ppbv to 40 ppbv. For specific projects lower calibration levels of 0.025 and 0.1 ppbv are included. The curve fit must be linear." Removed the statement from Section 12.2.18 "Or if project specific linear regression is required it will be used".	8/17/15

ATTACHMENT I: PRACTICAL QUANTIFICATION LIMITS (PQL), LIMIT OF QUANTIFICATION (LOQ) AND METHOD DETECTION LIMITS (MDL) FOR TARGETED VOLATILE ORGANICS

Analyte	CAS No.	PQL µg/m³	PQL ppbv	LOQ ppbv	MDLÔ ppbv
1,1,1-Trichloroethane	71-55-6	1.09	0.2	0.1	0.034
1,1,2,2-Tetrachloroethane	79-34-5	1.37	0.2	0.1	0.036
1,1,2-Trichloroethane	79-00-5	1.09	0.2	0.1	0.042
1,1-Dichloroethane	75-34-3	0.809	0.2	0.1	0.024
1,1-Dichloroethene	75-35-4	0.793	0.2	0.1	0.012
1,2,4-Trichlorobenzene	95-63-6	0.983	0.2	0.1	0.017
1,2-Dibromoethane	106-93-4	1.54	0.2	0.1	0.025
1,2-Dichlorobenzene	95-50-1	1.202	0.2	0.1	0.018
1,2-Dichloroethane	107-06-2	0.809	0.2	0.1	0.015
1,2-Dichloroethene (cis)	156-59-2	0.785	0.2	0.1	0.017
1,2-Dichloroethene (total)	540-59-0	0.810	0.2	0.1	0.017
1,2-Dichloroethene (trans)	156-60-5	0.810	0.2	0.1	0.017
1,2-Dichloropropane	78-87-5	0.924	0.2	0.1	0.036
1,3-Dichloropropene (cis)	10061-01-5	0.899	0.2	0.1	0.012
1,3-Dichloropropene (trans)	10061-02-6	0.899	0.2	0.1	0.035
1,4-Dichlorobenzene	106-46-7	1.202	0.2	0.1	0.034
1,4-Dioxane	123-91-1	1.799	0.5	0.5	0.074
2-Butanone	78-93-3	0.589	0.2	0.1	0.024
4-Methyl-2-pentanone	108-10-1	0.819	0.2	0.1	0.024
Acetone	67-64-1	0.475	0.2	0.2	0.031
Benzene	71-43-2	0.639	0.2	0.1	0.034
Bromodichloromethane	75-27-4	1.34	0.2	0.1	0.036
Bromoform	75-25-2	2.07	0.2	0.1	0.026
Bromomethane	74-83-9	0.769	0.2	0.1	0.015
Carbon disulfide	75-15-0	0.621	0.2	0.1	0.015
Carbon tetrachloride	56-23-5	1.258	0.2	0.1	0.031
Chlorobenzene	108-90-7	0.916	0.2	0.1	0.031
Chloroethane	75-00-3	0.523	0.2	0.1	0.022
Chloroform	67-66-3	0.965	0.2	0.1	0.015
Chloromethane	74-87-3	0.409	0.2	0.1	0.025
Dibromochloromethane	124-48-1	1.68	0.2	0.1	0.017
Ethylbenzene	100-41-4	0.867	0.2	0.1	0.036
Isopropylbenzene	99-87-6	2.45	0.5	0.1	0.022
Methyl tert-butyl ether	1634-04-4	0.720	0.2	0.1	0.017
Methylene chloride	75-09-2	0.687	0.2	0.2	0.061
Styrene	100-42-5	0.850	0.2	0.1	0.022
Tetrachloroethene	127-18-4	1.36	0.2	0.025	0.017
Toluene	108-88-3	0.753	0.2	0.1	0.025
Trichloroethene	79-01-6	1.07	0.2	0.025	0.022
Vinyl chloride	75-01-4	0.507	0.2	0.025	0.017
Xylene (total)	1330-20-7	0.868	0.5	0.1	0.036
1,2-dibromo-3-chloropropane **ò**	96-12-8				
1,2,3-trichlorobenzene **ò**	87-61-6				

ò Targeted TICs only.
Ô MDLs are determined annually.

ATTACHMENT II: EXAMPLE OF INSTRUMENT OPERATING PARAMETERS FOR TO-15 ANALYSIS

(Recommended program; modify as needed to optimize)

Sample Concentration

Sample Collection Flow-rate	100 mL/min
Sample Collection Time	Depending on sample volume
Sample Collection Flow-	100 mL/min
Glass bead Trap Temp. at Sample Collection / Desorption	-150°C / 10°C
Tenax Trap Temp. at Collection / Desorption	-50°C / 180°C
Cryo Focusing Trap Temp. at Collection / Desorption	-160°C / 50-90°C
Desorption Flow	1- 3 ml/min
Desorption Time	2 min

GC Conditions

Column	60 m x 0.32 mm ID, 1.0 µm film thickness, fused silica capillary column, RTX-1 Restek or equivalent
Carrier	Helium
Flow Rate	2.5 mL/min
Temperature Program:	Initial temp: 50°C Initial hold: 0 min Ramp 1: 9°C/min to 150°C Ramp 2: 30°C/min to 200°C Final Hold: 5.0 min

MS Conditions

Scan Mode

Manifold Temp:	240°C
Mass Range:	35 to 300
Scan Time:	0.38 sec
Number of scans:	1578
Threshold:	50
Minimum peak area:	1000

ATTACHMENT III: CHARACTERISTIC IONS FOR VOLATILE TARGETED COMPOUNDS

Analyte	Primary Ion*	Secondary Ion	Tertiary Ion
1,1,1-Trichloroethane	97	61	99
1,1,2,2-Tetrachloroethane	83	85	131
1,1,2-Trichloroethane	83	85	97
1,1-Dichloroethane	63	65	83
1,1-Dichloroethene	96	61	63
1,2,4-Trichlorobenzene	180	182	145
1,2-Dibromoethane	107	109	188
1,2-Dichlorobenzene	146	111	75
1,2-Dichloroethane	62	95	64
1,2-Dichloroethene (cis)	96	61	98
1,2-Dichloroethene (total)	96	61	98
1,2-Dichloroethene (trans)	96	61	98
1,2-Dichloropropane	63	112	41
1,3-Dichloropropene (cis)	75	77	110
1,3-Dichloropropene (trans)	75	77	110
1,4-Dichlorobenzene	146	111	75
1,4-Dioxane	88	58	43
2-Butanone**	43***	72	-
4-Methyl-2-pentanone	43	57	58
Acetone	43	58	-
Benzene	78	77	-
Bromodichloromethane	83	85	127
Bromoform	173	175	254
Bromomethane	94	96	-
Carbon disulfide	76	78	-
Carbon tetrachloride	117	119	-
Chlorobenzene	112	77	114
Chloroethane	64	66	-
Chloroform	83	85	47
Chloromethane	50	52	-
Dibromochloromethane	129	127	131
Ethylbenzene	106	91	105
Isopropylbenzene	105	120	-
Methyl tert-butyl ether	73	57	41
Methylene chloride	84	49	86
Styrene	104	78	103

Analyte	Primary Ion*	Secondary Ion	Tertiary Ion
Tetrachloroethene	164	129	166
Toluene	91	92***	-
Trichloroethene	95	130	132
Vinyl chloride	62	64	-
Xylene (total)	106	91	105
1,2-dibromo-3-chloropropane **ò**	75	155	157
1,2,3-trichlorobenzene **ò**	180	182	

* The primary ion should be used unless interferences are present, in which case, a second ion may be used.

** m/z 43 is used for quantification of 2-Butanone, but m/z 72 must be present for positive identification.

*** Quantitation ion differs from primary ion.

ò Targeted TICs.

ATTACHMENT IV: CHARACTERISTIC IONS FOR INTERNAL STANDARDS

Analyte	Primary Ion	Secondary Ion	Tertiary Ion
Bromochloromethane	128	49	130
1,4-Difluorobenzene	114	63	88
Chlorobenzene-d5	117	82***	119

*** Quantitation ion differs from primary ion.

ATTACHMENT V: BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass (m/z)	Ion Abundance criteria
50	8.0-40.0% of m/z 95
75	30.0-60.0% of m/z 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of m/z 95
173	Less than 2.0% of m/z 174
174	50-120% of m/z 95
175	4.0-9.0% of m/z 174
176	93.0-101.0% of m/z 174
177	5.0-9.0% of m/z 176

Note: All ion abundances must be normalized to m/z 95, the normal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

ATTACHMENT VI: SYSTEM MONITORING COMPOUND RECOVERY LIMITS

(Typical limits. Updated limits can be found in LIMS)

Compound	% Recovery
4-Bromofluorobenzene	70-130

ATTACHMENT VII: QUALITY CONTROL ACCEPTANCE CRITERIA AND CORRECTIVE ACTION PLAN

Parameter	Frequency	Acceptance Criteria	Corrective Action
BFB Tune	Daily (24 hour)	See Attachment V	• Identify the problem • Re-tune • MS tune criteria must be met before calibration
Initial Calibration	• Initially • Whenever required due to failure of CCV	• 5 points minimum • RSD < 30% • Allow 2 compounds out above 30% but below 40% RSD • No curve fits	• Recalibrate and verify before sample analysis • Prep new standards
ICV	• Following initial calibration	• All compounds must meet ±30% RSD	• If the requirements fail, reanalyze and recalibrate if necessary. • Sample analysis cannot begin until a compliant Initial Calibration and ICV meet acceptance criteria. • Samples analyzed after a non-compliant ICV must be reanalyzed.
Continuing Calibration Verification (CCV)	• Daily (24 hours) • Beginning of every batch	• All compounds must meet ±30% RSD	• If the requirements for continuing calibration are not met, reanalyze. • If a re-analysis of a CCV is still non-compliant, the standards preparation and equipment must be evaluated, prepare new standards if necessary and recalibrate.

Parameter	Frequency	Acceptance Criteria	Corrective Action
Internal Standard (IS)	• Added to all standards, samples, control samples, and method blanks prior to analysis	• Compounds o Bromochloromethane o Chlorobenzene-d5 o 1,4-Difluorobenzene • RT < 0.33 min daily std. • Response 60% to 140%	• If the criteria are not meet, in any of the samples, re-analysis is required demonstrate matrix interference. • If the criteria fails in any standard or method blank, than all the samples following the failed standard needs to be re-analyzed.
Surrogate	• Added to all standards, samples, control samples, and method blanks prior to analysis	• Compound o 4-Bromofluorobenzene • 70-130% recovery	• If % recoveries are outside the range, re-analysis is required, unless no positives are found and surrogate recovery was high. • If the sample re-analysis also fails the recovery criteria, report all data for the sample as "suspect".
Method Blank	• One per batch In a 24 hr tune period.	• Should not contain target analytes or interferences at concentrations that impact the analytical results for sample analyses. • Target analytes should not be greater than PQL.	• If the blank contains target analytes greater than the PQL, the blank needs to be re-analyzed. If the re-analysis passes criteria, then reanalyze the associated samples. • If the blank still fails, the system needs to be evaluated for the source of contamination and

Parameter	Frequency	Acceptance Criteria	Corrective Action
			affected samples re-analyzed. • If re-analysis of samples is not possible, report data flagged to indicate method blank contamination.
LFB	• One per batch in a 24 hr tune period. • Method specified compounds: Full Target List compounds	• 70-130% recovery	• Reanalyze • If a re-analysis of a LFB is still non-compliant, the standards preparation and equipment must be evaluated, prepare new • Re-analyze any positive samples in the batch after re-calibration.
Initial Demonstration of Capability (IDC)	• Per analyst; Before any samples are analyzed Analyze four replicates of a LFB • Method specified compounds: Full Target List compounds	• 70-130% recovery	• If requirements are not met evaluate standard preparation. • Reanalyze and recalibrate if necessary

APPENDIX A

Calibration and Verification of Sampling Equipment

Calibrating/Verifying the Flow of CS1200/Restricted Samplers

Attach a NIST traceable flow meter to the inlet of the sampler while the outlet is connected to a canister under vacuum and measure the flow.

Procedure:

1. Connect the correct restrictor to the inlet side of the CS1200 or the restricted sampler.
2. Connect the outlet to a canister that is at a vacuum of around 30”Hg.
3. Connect the Flow meter to the inlet.
4. Open the canister valve to start flow. Plug the inlet to the flow meter until the flow stops (no leaks.) Open the canister valve and the inlet of the flow meter and verify that flow restarts.

Verify the flow to the targeted flow for the samplers.

The flow on the CS1200 can be adjusted as follows:

5. Remove the tamper proof screw centered on the CS1200 body using a 1/8” hex key.
6. Adjust the set screw found under the tamper proof nut so that the flow agrees with the targeted flow. Note that very little adjustment should be necessary and flows should be ±10% of the desired set point.

APPENDIX B

Canister Sampling Guide

Pace Analytical®

Long Island Laboratory

Canister Sampling Guide

PROTECTING OUR ENVIRONMENT

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Table of Contents

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- Canisters that Pace Analytical utilizes are stainless steel containers that have had the internal surfaces coated with fused silica. This surface maintains chemical inertness, thus minimizing reactions with the sample and maximizing recovery of analytes from the canister.

- Canisters are spherical or cylindrical. The canister is prepared for sampling by evacuating the contents to a vacuum of approximately 29.9 inches of Mercury (in. Hg).

- Canisters can range in volume from less than 0.6 liter (L) to 15 L. 1.4 or 6 L canisters are generally used for ambient air samples. 0.6 L canisters are normally used for higher concentrations samples.

- Samples are collected by opening a valve allowing the sample to enter the canister. The valve is then closed and the canister is returned to the laboratory.

Canister Holding Times:

- Pace Analytical requires that canisters be returned within 14 days of receipt. Once a canister is cleaned, certified, and evacuated—it is recommend the canister be used for sample collection within 30 days.

Sample Hold Time:

- EPA Method TO-15 section 2.3 states that "storage times of up to thirty days have been demonstrated for many of the VOCs."

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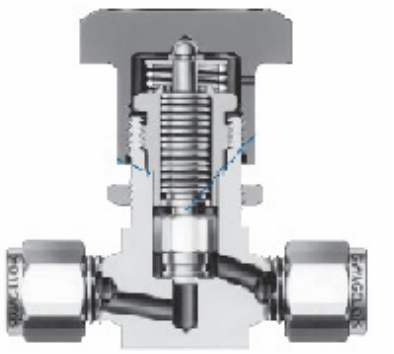
1.1) Associated Canister Hardware:

Associated hardware used with the canister includes the inlet valve and flow restrictor device, brass caps and plugs, particulate filter and vacuum gauge.

Valves:

- Canisters are fitted with either a 1/4" stainless steel bellows valve (Swagelok Nupro or Parker Hannifin), with 1/4". Swagelok male compression fittings or 1/4" or Entech Micro QT or "QT2" quick connect valves. These valves allow vacuum to be maintained in the canister prior to sampling and seal off the canister after sample collection.

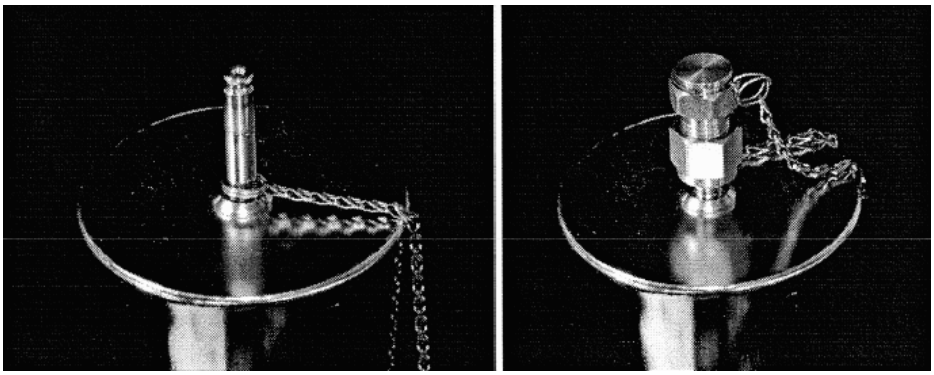
Bellows Valve



- Bellows Valves have metal-sealing surfaces that exhibit low potential for sample absorption and carryover. They are also referred to as "packless" because they utilize a welded bellows rather than an elastomeric seal to prevent leaks along the valve actuator.

- The Entech designed valve is a 1/4" tubular housing (QT - Quarter-inch Tube. The inclusion volume, or volume that is introduced when connecting to a sampling line, analyzer or test gauge, is 10 times smaller than in miniature quick connect valves and 80 times smaller that in Nupro valves.

EnTech QT2 Fittings:

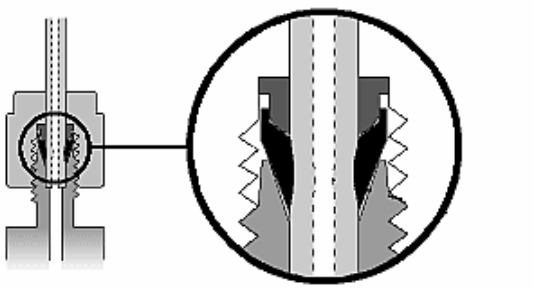


Valves connections:

- Compression fittings (i.e., Swagelok) seal by tightening with a wrench.

- QT2 fittings seal once they are connected.

Compression Fitting Showing Ferrule



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Valve Caps:

- Each canister comes with either brass cap (i.e., Swagelok 1/4" plug) or a two piece cap used on Micro QT Valves secured to the canister inlet. The cap serves two purposes. First, it ensures that there is no loss of vacuum due to a leaky valve or valve that is accidentally opened during handling. Second, it prevents dust and other particulate matter from entering the valve. (*Always replace the cap following canister sampling.)

Particulate Filter:

- Particulate filters should always be used when sampling with canisters.

Vacuum Gauge:

- A vacuum gauge is used to measure the initial vacuum of the canister before sampling and the final vacuum upon completion.

Entech Canister Cap

1/4" Plug

Guage w/QT2 Fitting

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There are two basic modes of canister sampling:

Grab and Integrated.

- A **grab sample** is taken over a short interval (< 1minute).
- An **integrated sample** is taken over an extended period (up to 24 hours or more).

Passive sampling utilizes the canister vacuum to draw sample into the canister.
Active sampling utilizes a pump to fill the canister.

- A 9/16,"7/16" and 1/2" wrenches may be necessary to connect and disconnect hardware.
- Compression fittings on the sampling hardware are 1/4" or 1/8". Swagelok.
- A wrench or quick connect fitting is used to connect to the canister.
- It is not necessary to over tighten the fittings; finger tight, plus 1/4 turn with a wrench, is sufficient. Bellows valves require no more than a half turn by hand to open or close the valve.
- Do not over-tighten the valve after sampling or it may become damaged.

Initial Vacuum of Canister:

- Canister vacuum must be checked prior to use and recorded the initial "Field Start" vacuum field of the chain of custody. Field sampling gauges are provided to check vacuum status and allow measuring of the change in canister pressure.
- The initial vacuum of the canister should be greater than 25" Hg.
- A canister vacuum of less than 25" Hg indicates that a leak exists and it should not be used.

Final Canister Vacuum:

- Final vacuum should be noted on the Final Vacuum "Field Stop" column on the chain-of-custody.
- If sample collection is ended while there is still vacuum in the can (e.g., 5" Hg), a leak check can be performed when the lab receives the canister by verifying the canister vacuum. Samples can be collected either by allowing the canister to reach ambient conditions or by leaving some residual vacuum (e.g., 5" Hg) in the canister. If the canister vacuum is greater than 5" Hg (i.e., more vacuum), the canister may need to be pressurized prior to analysis. This may result in elevated reporting limits.

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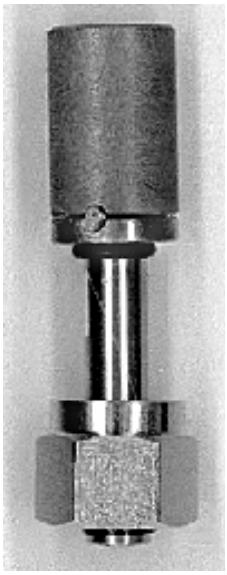
2.1) Procedures for Canister Grab Sampling:

1/4 Compression Fitting Filter



2.1.1) Canisters with compression fittings:

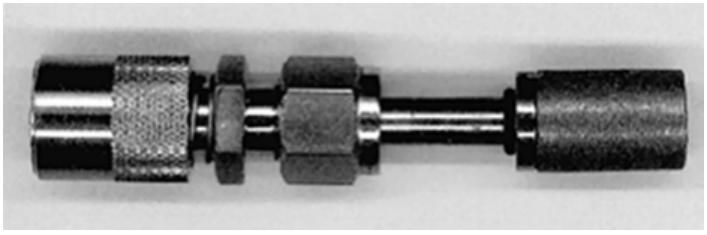
1. Verify that valve is closed.
2. Open and close valve.
3. Read vacuum on the gauge.
4. Record gauge reading on "Field Start" column of chain-of-custody.
5. Verify that canister valve is closed.
6. Remove the brass cap.
7. Attach grab sampling filter and allow sufficient time for filling of the canister.
8. Close valve by hand tightening knob clockwise.
9. Replace the brass cap.
10. Verify and record "Field Stop" final vacuum of canister.
11. Fill out canister sample tag.

2.1.2) Canisters with Quick connect fittings (QT2):

Female QT2 Fitting

1. Remove two piece cap.
2. Attach a pressure gauge by holding the gauge in one hand; slide back the knurled collar with thumb and index finger. Hold the canister in the other hand with protective end cap removed and with tip of canister facing the gauge.
3. Insert the canister tip into the gauge and release the knurled collar.
4. Read vacuum on the gauge.
5. Record gauge reading on Initial "Field Start" vacuum column of chain-of-custody.
6. Attach grab sampling filter and allow sufficient time for filling of the canister.
   a) Filter will either have a QT2 fitting or a design that must be held in place by hand.
7. Remove grab sampling filter.
8. Reattach a pressure gauge.
9. Record final vacuum "Field Stop" of canister.
10. Fill out canister sample tag.

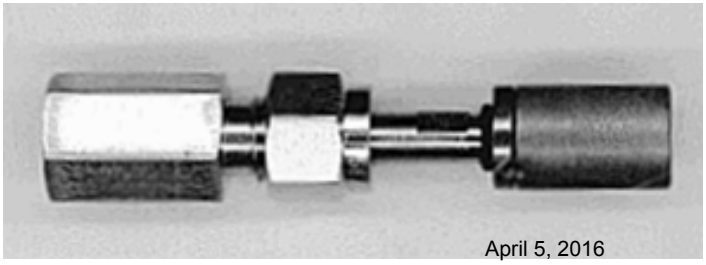
1/4 QT2 Fitting Filter



Return canister in the packaging.
Fill out chain-of-custody.
Place chain-of-custody in box and retain yellow copy.

*** Record the Canister Serial Number on the chain of custody.**

Handheld QT2 Fitting Filter



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- When samples are collected over a length of time, the sample concentration is the average of the concentration over that time period.
- Flow controllers or restrictors are devices that regulate the flow of air during sampling into a canister. These devices enable a sampling at a pre-set flow rate and sampling time period.
- Sampling Time and Flow Controller Setting must be specified in advance so that the flow controllers can be pre-set by the lab prior to shipment.

Critical Orifice Device

A critical orifice flow restrictor maintains constant flow until the pressure differential across the orifice is less than a 1:2 ratio. To provide true time weighted sampling sample collection should stop at the 50% of the canister volume. Larger volumes may be collected if sample true averaging over the entire sampling time is not critical.

Constant Pressure Control With Critical Orifice

Constant Pressure Flow controller provides time weighted sampling with a pressure controller and critical orifice. Compensation for changes in canister pressure is made to maintain a constant pressure differential across the critical orifice so that a constant flow rate can be maintained for a larger percentage of the canister volume.

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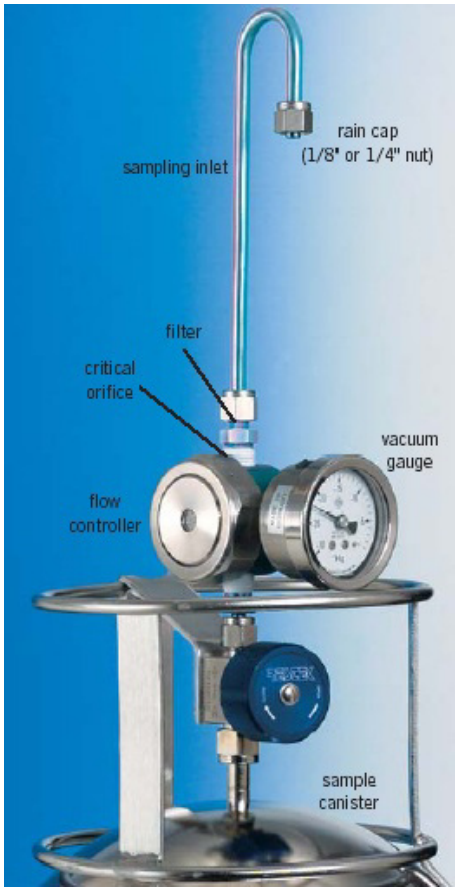
2.2.1) Procedures for Integrated Sampling:

2.2.1.1) Canisters with compression fittings:

1. Verify that valve is closed.
2. Open and close valve.
3. Read vacuum on the canisters gauge.
4. Record gauge reading on Initial Vacuum "Field Start" column of chain-of-custody.
5. Verify that canister valve is closed.
6. Remove the brass cap from the canister.
7. Attach the flow controller to the canister.
8. Remove the cap or plug from the top of the flow controller.
9. If sampling a sample source via tubing, connect the tubing to the 1/4" connection on the flow controller's inlet.
10. The canister valve can now be opened, allowing the can to fill.
    a) The filling can be monitored by observing the canister pressure.
11. Record the final canister "Field Stop" vacuum.
12. After sampling close the canister valve, remove the flow controller and replace the brass cap.
13. Fill out canister sample tag.

Flow Controller w/Compression Fitting



1/4 Compression Plug

Return canister in the packaging.
Fill out chain-of-custody.
Place chain-of-custody in box and retain yellow copy.

*** Record the Canister and Flow Controller Serial Numbers on the chain of custody.**

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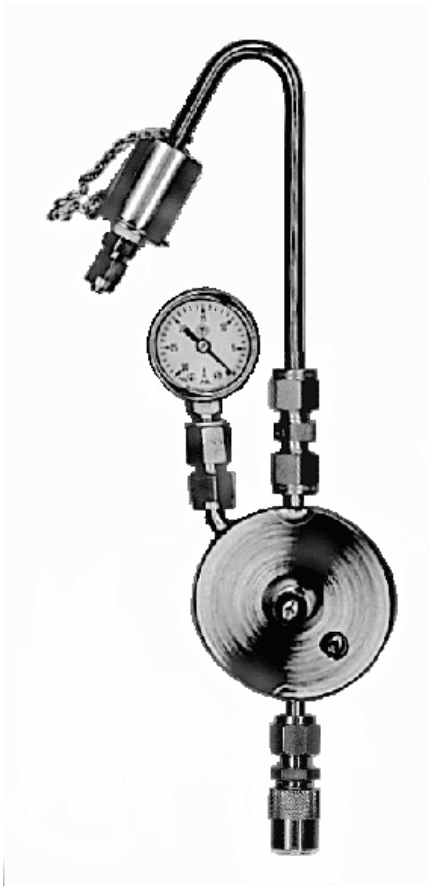
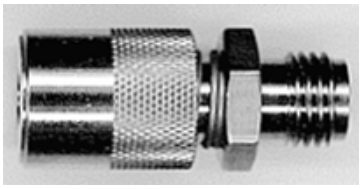
CS1200 Flow Controller w/QT2



2.2.1.2) Canisters with Quick connect fittings (QT2):

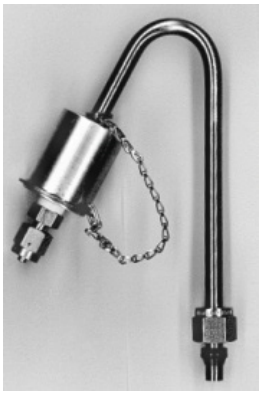
1. Remove two piece cap from the canister.
2. Attach a pressure gauge by holding the gauge in one hand; slide back the knurled collar with thumb and index finger. Insert the canister tip into the flow controller, and release the knurled collar.
3. Read vacuum on the gauge.
4. Record gauge reading on Initial Vacuum "Field Start" column of chain-of-custody.
5. Remove 1/8 in. compression fitting at flow controller inlet with a 7/16 in. wrench (leave cap connected to retaining chain).
6. If sampling a sample source via tubing, connect the tubing to the 1/8 in. connection on the flow controller's inlet.
7. Attach quick connect (QT2) flow controller to the canister.
8. Allow sufficient time for filling of the canister.
9. Sampling progress can be monitored by observing the gauge on the flow controller or, if present, the gauge on the canister.
10. Record final vacuum "Field Stop" of canister.
11. Remove the flow controller from the canister.
12. Replace two piece cap on the canister.
13. Fill out canister sample tag.

Female QT2

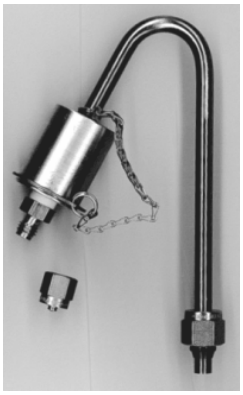


CS1200 sampler top showing 1/8 compression (Swagelok) fitting:

1) Attached



2) Removed



3) Filter Cover Removed

Return canister in the packaging.
Fill out chain-of-custody.

Place chain-of-custody in box and retain yellow copy.

*** Record the Canister and Flow Controller Serial Numbers on the chain of custody.**

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3.0) Equipment Fees / Notes

Return canisters in boxes provided.

Unreturned equipment charges:

- **Canisters: $305 - $850**
- **Flow controllers: $120 - $750**
- **Pressure gauges: $150**

4.0) Example Chain of Custody:

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(sequential #'s)

AIR CANISTER CHAIN OF CUSTODY

Client Contact Information	Project Manager:	CLIENT:	H2M SDG NO.:
Company:	Phone:	Samplers Name(s)	
Address:	Site Contact:		
City/State/Zip			
Phone:			
FAX:			
Project Name:	Analysis Turnaround Time		
Site:	Standard (Specify)		
PO #	Rush (Specify)		

				Canister Pressure								Analysis				Matrix			
				FIELD		LAB													
Sample Identification	Date Collected	Time Collected	Temp. (F)	Initial("Hg) (Start)	("Hg) / PSI (Stop)	Outgoing ("Hg) (Lab)	Incoming ("Hg) (Lab)	Flow Controller ID	Canister ID	Can Size (L)	LAB ID No.	TO-15	OTHER			Indoor / Ambient Air	Soil Gas	Source Level	

	Pressure				Temperature (Fahrenheit)			
	Ambient	Maximum	Minimum		Ambient	Maximum	Minimum	
Start				Start				
Stop				Stop				

Special Instructions/QC Requirements & Comments:

Samples Relinquished by:	Date/Time:	Received by:	Date/Time:
Relinquished by:	Date/Time:	Received by:	Date/Time:

WHITE COPY - ORIGINAL YELLOW COPY - CLIENT PINK COPY - LABORATORY

* Notify lab if equipment is damaged upon receipt. Client is responsible for damage to equipement

STANDARD OPERATING PROCEDURE

Volatile Organics Compounds
Methods: EPA 8260B & 8260C

SOP NUMBER:	PGH-O-015-9
REVIEW:	Tim Harrison
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-O-015-8
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager — 08/14/15 Date

Senior Quality Manager — 08/14/15 Date

Department Manager/Supervisor — 08/14/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This SOP describes the procedure to be followed for the GC/MS analysis of volatile organic compounds by EPA Methods 8260B and 8260C.

2. Scope and Application

2.1 This method is restricted to use by, or under the supervision of analysts experienced in the operation of a purge and trap system, a gas chromatograph/mass spectrometer, and in the interpretation of mass spectral data.

2.2 Tables 2 and 4 contain the standard Pace Analytical target compound lists (TCL) for aqueous and solid samples, respectively, as well as additional compounds that may be determined by this method along with the typical reporting limits for each analyte listed. However, lower reporting limits can be used based on the individual method detection limits for each instrument.

2.3 This procedure is used to determine the presence and concentration of volatile organic compounds (VOC) in a variety of matrices. The method is applicable to nearly all types of samples: ground and surface water, aqueous sludge, waste solvents, oils, tars, filter cakes, spent carbons, soil, sediments, and TCLP extracts. The most commonly used purge and trap techniques for volatile organic analytes (VOA) in aqueous samples is (are) Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples).

2.4 In this SOP, the term ‘VOA’ and ‘VOC’ are used interchangeably.

3. Summary of Method

3.1 For aqueous analysis, nitrogen is bubbled through a 5 mL-water sample contained in a specially designed purging chamber.

3.2 For low-level soils, the nitrogen is bubbled through the 40mL VOA vial that contains 5g of soil and 5mL of deionized water.

3.3 For a medium level soil, a measured amount of soil is collected and extracted in methanol. A portion of the methanol is then taken and diluted into a 40mL VOA vial where it is treated like a water sample.

3.4 In each case, the purgeable compounds are transferred from the aqueous phase to the vapor phase. The vapor is then swept through a sorbent trap where the purgeables are trapped. After purging is complete, the sorbent trap is heated and back flushed with helium to desorb the compounds onto a chromatographic column. The gas chromatograph is temperature programmed to separate the compounds, which are then detected by the mass spectrometer.

4. Interferences

4.1 Major sources of contamination include solvent vapors in the laboratory, impurities in the nitrogen purging gas, and with the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) sealants, tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When interference peaks are noted in the blanks, the purge gas source should be replaced. When compounds such as ketones are found in the blanks, the sorbent trap may need to be replaced.

4.2 In order to minimize the common problem of laboratory air contamination due to compounds such as methylene chloride and acetone, the following steps should be taken:

4.2.1 Volatile GC/MS systems are kept in a room in a separate part of the building from the organic extractions department.

4.2.2 The ventilation system is designed to maintain positive pressure in the volatiles laboratory. This forces a constant flow of air out of the room and limits the flow of contaminated air into the room.

4.2.3 All volatile samples are stored in refrigerators dedicated to the department.

4.2.4 All standard solutions are stored in a separate refrigerator/freezer from samples. This prevents the diffusion of volatile compounds through the VOA vial septa.

4.2.5 Standard solutions and samples containing high analyte concentrations are prepared in the fume hood.

4.3 Samples can be contaminated by diffusion of volatile compounds through the septum seal during handling and storage. A trip blank prepared from organic free water and carried through the entire sampling, handling and storage procedures can serve as a check for contamination.

4.4 Contamination may also occur when a sample containing low concentrations of VOCs is analyzed immediately after a sample containing high concentrations of VOCs. After the analysis of a sample containing high concentrations of VOCs, one or more blanks may be analyzed to check for carryover. Since the history of every sample analyzed is not known, a blank cannot always be analyzed after a high concentration sample. If a sample analyzed immediately following the high concentration sample does not contain compounds present in the high level sample, freedom from contamination has been established.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions of the common laboratory terms used throughout this SOP.

6.2 VOC: Volatile Organic Compounds

6.3 TCLP: Toxicity Characterization Leaching Procedure

6.4 ZHE: Zero Headspace Extraction

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Sample Collection: Sample collection varies according to the sample matrix.

8.1.1 Aqueous samples should be poured into a 40mL VOA vial without introducing any air bubbles within the vial as it is being filled.

8.1.1.1 At least two VOA vials should be filled and labeled immediately upon sample collection.

8.1.1.2 The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial is inverted, no headspace is visible.

8.1.1.3 The sample should be hermetically sealed at the time of sampling, and must not be opened prior to analysis in order to preserve sample integrity.

8.1.1.3.1 The presence of bubbles in a sample vial indicates either improper sampling technique or a source of gas evolution within the sample.

8.1.1.3.2 In general, any bubbles smaller than 6 mm will not adversely affect volatile data.

8.1.1.3.3 If bubbles are noted to be larger than 6 mm, the analyst should note this finding in the final report.

8.1.2 Waste and oil samples may be collected in 40mL VOA vials or any suitable glass container.

8.1.3 There are several options available for collection and preservation of soil and aqueous sample. See Appendix 3 for details.

8.1.4 Refer to EPA Method 5035 & 5035A for further information.

8.2 Preservation

8.2.1 Aqueous samples must be preserved with hydrochloric acid (HCl) to adjust the pH to less than 2.0. See Apenndix 3 for detailed preservation requirements.

8.2.1.1 The VOA vials are purchased with hydrochloric acid added by the manufacturer C&G part number NC0152162, or equivalent.

8.2.2 Waste and oil samples do not require preservation.

8.2.3 Low level soil samples can be preserved with sodium bisulfate, see Appendix 3 of this SOP.

8.2.4 Medium Level soil samples are preserved with purge ant trap grade methanol. See appendix 3 of this SOP.

8.2.5 Refer EPA to Method 5035A and Appendix 3 for soil preservation techniques.

8.3 Shipment: Samples received by the laboratory are checked for temperature upon receipt. Samples should be received on ice at ≤6°C. If samples arrive with temperature readings outside this range, it will be documented (on the SCUR) and in the project file.

8.4 Storage: Samples must be analyzed within 14 days of collection. If samples are analyzed outside of holding time, it must be documented in the final report. All volatile samples are stored refrigerated at ≤6°C from the time of receipt until 30 days after analysis. After 30 days, the aqueous samples are disposed of in the laboratory waste streams.

8.4.1 If the sample is received unpreserved the holding time is 7 days.

9. Equipment and Supplies

9.1 Purge and Trap Device: Tekmar Model LCS 3000, or equivalent, with Supelco Vocarb 3000® trap, or equivalent.

9.1.1 EST Environmental PT^2 system.

9.2 Autosampler: EST Environnemental Archon Model 8100, EST Environnemental Centurion, or equivalent.

9.3 Gas Chromatograph: Hewlett Packard Model 6890, or equivalent.

9.4 Mass Spectrometer: Hewlett Packard Model 5973, or equivalent.

9.5 Capillary Column: Restek RTX-VMS, 20m X 0.18mm diameter column, or equivalent.

9.6 Sample containers: 40mL VOA vials with PTFE septa.

9.7 Data System:

9.7.1 Hewlett Packard Enviroquant®. Used for operation of the GC/MS system.

9.7.2 ThruPut Target®. Used for the acquisition of data and processing of mass spectral information. The data system is equipped with EPA/NIST Mass Spectral Library.

9.8 Balance: Mettler Model AE 240, capable of weighing to 0.0001g, or equivalent.

9.9 Spatulas: Stainless Steel.

9.10 Syringes: Hamilton Gastight syringes ranging from 10mL to 25mL.

9.11 Volumetric Flasks: Class A ranging from 5mL to 1000mL, glass.

9.12 pH paper: Wide range Whatman Type CF, or equivalent.

9.13 Mininert Vials: Supelco 1.0mL, 5.0mL and 10.0mL, or equivalent.

9.14 VOA vials: I-CHEM 40mL glass container with a PTFE-lined septum and an open top screw-cap, or equivalent.

9.15 Magnetic stir bars: PTFE or glass coated 12mm x 4mm.

9.16 Encore™ Sampler: field core sampling / storage container, or equivalent.

9.17 Ottowa sand: purified solid matrix. Fisher brand, or equivalent.

9.18 Repipette dispensers: Lab Industries, Inc. or equivalent, 20mL and 50mL, accuracy up to 1% and reproducible to 0.15 at full scale.

10. Reagents and Standards

10.1 Methanol: Fisher Brand Purge and Trap grade, or equivalent.

10.2 Organic-Free reagent water: Millipore Super Q-ASTM Type II, DI, or equivalent.

10.3 Hydrochloric Acid (1:1 v/v) HCl: Prepared by carefully adding a measured volume of concentrated HCl to an equal volume of DI water.

10.4 Initial Calibration Stock Solutions (ICAL): Purchased as certified solutions. All standards are stored in a freezer between -10°C and -20°C. All standards are purchased with an expiration date of at least six months: Stock standards are disposed of after six months or more frequently if degradation is noted. Initial stock solutions are stored in 1mL, 5mL, or 10mL Mininert vials. Using a syringe, prepare stock solutions as follows: (Refer to the Volatiles Department Standard Logbook for the specific instructions on how to prepare each of the standards and reagents listed below.)

10.4.1 Volatiles Mix: Received as a certified solution from NSI Solutions, Inc. (Catalog Number C-349H-12) at 2000μg/mL and diluted with DI water to a working standard of 200μg/mL in a 10mL volumetric flask.

10.4.2 Mix A: Received as a certified solution from NSI Solutions, Inc. (Catalog Number Q-4937.) All of the compounds in the mix are 2000µg/mL, except Cyclohexanone, 2-Nitropropane, 1,4-dioxane, iodomethane, acetonitrile, isobutanol, allyl chloride and t-butanol. These compounds' concentrations are 10000µg/mL, except 1,4-dioxane which is 20000µg/mL. The working standard is prepared by performing a 1:10 dilution with DI water using a 10mL volumetric flask.

10.4.3 Gases Mix: Received as a certified solution from NSI Solutions, Inc (Catalog Number C-303H) at 2000μg/mL and diluted to 200μg/mL with DI water using a volumetric flask.

10.4.4 Vinyl Acetate: Received as a certified solution from Restek (Catalog Number 30216) at a concentration of 2000μg/mL and diluted to 200μg/mL with DI water in a volumetric flask. This mix can be diluted with the Gases Mix to reduce the number of solutions required to make daily standards and calibration curves.

10.4.5 Acrolein: Received as a certified solution from AccuStandard (Catalog Number APP-9-007-10X) at a concentration of 1.0mg/mL and diluted to 200μg/mL using a volumetric flask. This mix can be diluted with 2-chloroethyl vinyl ether to reduce the number of solutions required to make daily standards and calibration curves.

10.4.6 2-chloroethyl vinyl ether: Received as a certified solution from NSI Solutions, Inc. (Catalog Number 0017P) at 1.0mg/mL and diluted to 200μg/mL using a

volumetric flask. This mix can be diluted with acrolein to reduce the number of solutions required to make daily standards and calibration curves.

10.4.7 Ethanol: Received as a certified solution from Restek (Catalog Number 30466) at a concentration of 10,000µg/mL and diluted to 2000µg/mL using DI water in a volumetric flask.

10.4.8 2-methylnaphthalene: Received as a certified solution from Restek (Catalog Number 563021) at 2000µg/mL and diluted to 200µg/mL using a volumetric flask. This mix can be diluted with the Volatiles Mix to reduce the number of solutions required to make daily standards and calibration curves.

10.5 Prepare working initial calibration solutions of 1, 4,10, 20, 50, 200, and 400µg/L for aqueous and 5, 10, 20, 50, 100 and 400µg/L for solids by adding the appropriate amount of each of the above stock solutions to a 100mL volumetric flask containing DI water.

10.5.1 The flask should be filled halfway up the neck to allow for adjustment to 100mL after standards have been added.

10.5.2 Final adjustment is accomplished by adding DI water using a disposable pipette.

10.5.3 The volumetric flask is then sealed and inverted three times to mix. Standards are transferred to labeled 40mL VOA vials and refrigerated at ≤6°C.

10.5.3.1 t-butanol, allyl chloride, iodomethane, cyclohexanone, 2-nitropropane, 1,4-dioxane, acetonitrile, isobutanol and m,p-xylenes vary from the concentrations listed above. The concentrations of t-butanol, allyl chloride, iodomethane, cyclohexanone, 2-nitropropane, acetonitrile and isobutanol are 5, 20, 50, 100, 250, 1000 and 2000µg/L for aqueous sample analysis and 25, 50, 100, 250, 500, 2000µg/L for solid sample analysis.

10.5.3.2 The concentration of 1,4-dioxane and ethanol are 10, 40, 100, 200, 500, 2000, 4000µg/L for aqueous samples and 50, 100, 200, 500, 1000, and 4000µg/L for solid samples. The concentration of m,p-xylene is 2, 8, 20, 40, 100, 400, and 800µg/L for aqueous samples and 10, 20, 40, 100, 200, and 800µg/L for solid samples.

10.6 CCV Standard preparation procedure.

10.6.1 Add the following aliquots of standard(s) to a 100mL volumetric flask that contains ~85mL DI water.

- 25uL of the Gases/Vinyl Acetate Mix.
- 25uL of the VOA Mix A.
- 25uL of the Ethanol Mix.
- 25uL of the 2-Methylnaphthalene/Volatiles Mix, and,
- 25uL of the Acrolein/2chloroethylvinyl ether Mix.

10.6.2 Dilute to volume with DI water. Stopper the flask and mix by inverting three times.

10.6.3 Discard the volume of CCV standard in the neck of the volumetric flask and gently pour (with minimal agitation) the solution into two labeled 40mL VOA vials.

10.7 Continuing Calibration Standard (CCAL): Prepare a daily continuing calibration standard at a 50µg/L concentration. The CCAL may be prepared from the same stock solutions as the ICAL. CCAL standards are kept refrigerated at ≤6°C.

10.8 Surrogate Standards: Toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4 and dibromofluoromethane. Each sample undergoing GC/MS analysis must be spiked with surrogate standard solution prior to analysis. Prepare surrogate standards at an appropriate concentration determined by the loop calibration of Archon or Centurion autosampler (Appendixes 1 and 2). The Archon is programmed to inject *approximately* 1.0μL, the Centurion is programmed to inject *approximately* 10.0μL, of this standard into each 5mL or 5g sample to achieve a concentration in the sample of 30μg/L. Standards are stored in a freezer between -10°C and -20°C.

10.8.1 Surrogate 1,2-dichlorobenzene-d4 is added to water samples by the Centurion to one concentrator only. This surrogate is used as a marker only and is not evaluated for recovery.

10.9 Internal Standards: Fluorobenzene, Chlorobenzene-d5, and 1,4-Dichlorobenzene-d4. Each sample undergoing GC/MS analysis must be spiked with internal solution prior to analysis. Prepare internal standards at an appropriate concentration determined by the loop calibration of Archon or Centurion autosampler (Appendix 1). The Archon is programmed to inject approximately 1.0μL, the Centurion is programmed to inject approximately 10.0μL, of this standard into each 5mL or 5g sample to achieve a concentration in the sample of 30μg/L. Standards are stored in a freezer between -10°C and -20°C.

10.10 Tuning Standard (BFB): Surrogate standard mix, which contains BFB. The Archon or Centurion autosampler can be programmed to add the surrogate mix to organic-free reagent water, resulting in a concentration of 30μg/L. Standards are stored in a freezer between -10°C and -20°C

10.11 Laboratory Control Sample Stock Solutions (LCS): Purchased as certified solutions. All standards are stored in a refrigerator at ≤6°C. All standards are purchased with an expiration date of at least six months. Stock standards are disposed of after six months or more frequently if degradation is noted. Initial stock solutions are stored in 1mL, 5mL, or 10mL Mininert vials. Using a syringe, prepare stock solutions as follows:

10.11.1 2-Chloroethyl vinyl ether: Received as a certified solution from Restek (Catalog Number 30265) at a concentration of 2000μg/mL and diluted to 200μg/mL using a volumetric flask.

10.11.2 Custom Mix (Alcohols/Ethers): Received as a certified solution from Restek (Catalog Number 567034) at a concentration of 2000μg/mL and diluted to 200μg/mL using a volumetric flask.

10.11.3 Acrolein Mix: Received as a certified solution from Restek (Catalog Number 30645) at a concentration of 2000μg/mL and diluted to 200μg/mL using a volumetric flask. This mix can be diluted with the Gases Mix to reduce the number of solutions required to make the Laboratory Control Sample.

10.11.4 502.2 Megamix: Received as a certified solution from Restek (Catalog Number 30431) at a concentration of 2000μg/mL and diluted to 200μg/mL using a volumetric flask.

10.11.5 Gases Mix: Received as a certified solution from Restek (Catalog Number 30042) at a concentration of 2000μg/mL and diluted to 200μg/mL using a volumetric flask. This mix can be diluted with Chloroprene to reduce the number of solutions required to make the Laboratory Control Sample.

10.11.6 Chloroprene: Received as a certified solution from Supelco (Catalog Number 46869-U) at a concentration of 2000μg/mL and diluted to 200μg/mL using a volumetric flask. This mix can be diluted with the Gases Mix to reduce the number of solutions required to make the Laboratory Control Sample.

10.11.7 2-Methylnaphthalene: Received as a certified solution from AccuStandard (Catalog Number S-518B) at a concentration of 2000µg/mL and diluted to 200µg/mL using a volumetric flask. This mix can be diluted with the 502/524 Mix to reduce the number of solutions required to make the Laboratory Control Sample.

10.11.8 Ethanol: Received as a certified solution from Accustandard (Catalog Number M-8015B/5031-11) at a concentration of 10000µg/mL and diluted to 2000µg/mL using a volumetric flask. This mix can be combined with Custom Mix (Alcohols/Esters) to reduce the number of solutions required to make the Laboratory Control Sample.

10.11.9 VOA Cal Mix 1 (Ketones): Received as a certified solution from Restek (Catalog Number 30006) at 5000µg/mL and diluted to 200µg/mL using a volumetric flask.

10.12 Laboratory Control Sample (LCS): Solutions are received as certified solutions and are prepared by performing a 1:10 dilution using a 10mL volumetric flask. All target analytes are included in the LCS. The daily LCS is prepared by diluting 10µL of each of the solutions into 100mL of reagent water. The LCS has an expected concentration of 20µg/L Standards are stored in a freezer between -10°C and -20°C.

10.13 Matrix Spike (MS/MSD) Standards: Matrix spiking standards should be prepared from volatile organic compounds which is representative of the compounds being investigated. All target analytes are included in the matrix spike. The spiking solutions are prepared from a separate source than used for the calibration standards. Samples are spiked the same as the LCS and yield an expected concentration of 20µg/L. Standards are stored in a freezer between -10°C and -20°C.

10.14 Second source standards/ICV: These standards are purchased and prepared from a separate source than the calibration standards.

10.15 All standard stock solutions prepared by the analyst shall be documented in a standard logbook, located in the Volatiles laboratory. Entries must include a unique identification number for each standard material prepared along with the purity or concentration of the stock used, the lot number of both the material used and any solvents used to prepare the solution, the amount of stock or material used, the final volume of the solution generated, the final concentration of the solution, the date the solution was prepared and the initials of the analyst responsible for preparing the solution.

11. Calibration

11.1 Instrument Operating Conditions - Operating conditions are variable to allow for optimum analytical results. Each instrument has specific conditions that give optimal results. The following are the typical ranges of analytical conditions:

11.1.1 Purge and Trap

Purge gas	Helium or Nitrogen
Purge Time	11.0 ± 0.1 minutes
Purge Flow Rate	≈ 45 mL/min
Purge Temperature:	Ambient for water & medium level soil samples. 40°C for low level soil samples
Desorb Temperature:	250°C
Desorb Flow Rate:	60 mL/min
Desorb Time:	0.5 minute ± 0.1 minutes
Bake Time:	5-10 minutes
Bake Temperature:	270°C

11.1.2 Gas Chromatograph

Carrier Gas:	Helium or Hydrogen
Initial Temperature:	45°C
Initial Hold Time:	3.5 minute
Ramp Rate 1:	60°C/minute
Final Temperature 1:	120°C
Final Hold Time 1:	0 minutes
Ramp Rate 2:	30°C/minute
Final Temperature 2:	240°C
Final Hold Time 2:	hold until 2-methyl naphthalene elutes
Injection Port Temperature:	220°C

11.1.3 Mass Spectrometer

The following are required analytical conditions:

Electron Energy:	70 electron volts
Mass Range:	35-300 amu
Scan Time:	To give at least 5 scans per peak, not to exceed 2 seconds per scan

Tuning: Each instrument must be hardware-tuned to meet the criteria specified below for BFB. Analyses must not begin until these criteria are met. Prepare the BFB standard and analyze it on the Archon or Centurion. The instrument performance check solution (BFB) must be analyzed once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The 12-hour period begins at the time of BFB injection and ends after exactly 12 hours have elapsed according to the system clock. All sample injections must start prior to the end of the 12-hour period.

Mass	m/z Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	Less than 2% of mass 174
174	50% or greater of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

11.1.4 Acquire the mass spectrum of BFB averaging three scans (the peak apex scan and the scans immediately preceding and following the apex). A background subtraction must be done using a single scan no more than 20 scans prior to the peak. Do not background subtract part of the BFB peak. If the technical criteria are not met, retune the GC/MS. It may also be necessary to clean the ion source or take other corrective actions.

11.1.5 All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

11.2 Initial Calibration (ICAL): Operate the GC/MS system according to the manufacturer's instructions. Analyze all of the ICAL standards prepared. Program the Archon or Centurion to add internal standard to each separate aliquot of the calibration curve.

11.2.1 A minimum of five calibration points is required for linear curves, and six for 2nd order calibration curves.

11.2.1.1 Higher order curve equations for calibrations must meet the requirements as listed Sections 7.5.2 and 7.5.3 of EPA Method 8000. Unless there is prior knowledge regarding a parameter, the lower order calibration curves are to be used for the Initial Calibration of the instrument. Increasingly, more complex models are to be used only after the lower order equations are shown not to work. In all instances, the higher order calibration curves are not to be used as a means for not performing system maintenance.

11.2.2 **Removal of Points from a Calibration Curve**:

11.2.2.1 Removing or replacing of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. The curve is evaluated with the levels removed. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve must be reanalyzed. Corrective action may include instrument maintenance and/or repreparation of standards. If the low standard is dropped, then the lowest remaining calibration point must be at or below the reporting limit.

11.2.3 The same calibration model used for the initial calibration must be used for all subsequent analyses of standards and reagents until the next initial calibration. The model utilized can not be changed after the ICAL has been processed and approved.

11.2.4 Separate initial calibration curves must be performed for unheated (aqueous/methanol extracted) and heated (low-level soil) samples.

11.2.5 Separate initial calibration curves must be run per concentrator for Centurion and PT[2] systems.

11.2.6 The system software will calculate response factors (RF) for each compound in each standard according to the following calculation:

$$RF = (A_s \times C_{is}) / (A_{is} \times C_s)$$

Where:
A_s = Peak area of the analyte or surrogate
A_{is} = Peak area of the internal standard
C_s = Concentration of the analyte or surrogate
C_{is} = Concentration of the internal standard

11.2.7 Average RFs are calculated for each compound using the equation:

$$Average\ RF = \Sigma\ individual\ RFs\ /\ number\ of\ standards.$$

11.2.8 Using the calibration standards, the system software will calculate the percent relative standard deviation (%RSD) for each compound using the following equation:

$$\%RSD = (RF_{SD} \times 100) / RF_{avg}$$

Where:
RF_{SD} = Standard deviation of the five RFs for each compound
RF_{avg} = Average of the RFs for each compound

11.2.9 Standard Deviation (S)

$$S = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{(n-1)}}$$

Where
n = number of data points
X_i = individual data point
$\overline{X}$ = average of all data points

11.2.10 Linearity of target analytes:

11.2.10.1 **For Method 8260B**: If the %RSD of any target analyte is 15% or less, then the response factor may be assumed to be constant over the calibration range, and the average response factor may be used for the quantitation of samples.

11.2.10.1.1 If the %RSD is greater than 15%, another calibration model may be used. The other models are linear calibration and quadratic calibration.

11.2.10.1.2 When using models other than average RF, the origin (0,0) must not be included in the calibration curve. Performing a linear regression ($r \geq 0.99$ or better) or a weighted least squares regression ($r \geq 0.99$ or better) must be employed to achieve linearity. A weighted curve is often recommended, unweighted regressions are likely to have high relative errors at the lower concentration levels and are strongly discouraged. Weighted regressions should be used whenever possible. The correlation coefficient (r) must be ≥ 0.99 when using linear regression.

11.2.10.1.3 For 2nd order curves such as quadratic the coefficient of determination (COD) must be ($r^2 \geq 0.99$ or better). Second order curves should only be used in circumstances where a linear curve is clearly not appropriate. While quadratic curves are generally reliable within the calibration range, they can produce highly erroneous results above the calibration range, including negative numbers at high concentrations. If a quadratic curve is used, each and every calibration plot must be visually inspected to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal

11.2.10.1.4 When calculating the calibration curve using the linear regression model and 2nd order quadratic, the calibration curve must be evaluated at the lowest concentration calibration standard. The lowest standard is requantitated. The results should be between 70% and 130% recovery of the true value. This low standard evaluation must be kept with the calibration data.

11.2.10.2 **For Method 8260C**: If the %RSD of any target analyte is 20% or less, then the response factor may be assumed to be constant over the calibration range, and the average response factor may be used for the quantitation of samples.

11.2.10.2.1 If the %RSD is greater than 20%, another calibration model may be used. The other models are linear calibration and quadratic calibration.

11.2.10.2.2 When using models other than average RF, the origin (0,0) must not be included in the calibration curve. The correlation coefficient (r) must be ≥ 0.99 when using linear regression and COD or r^2 ≥ 0.99 when using quadratic regression.

11.2.10.2.3 Method 8260C: It is also recommended that the minimum response factor for the most common target analytes as noted in Table 10, be demonstrated for reach individual calibration levels as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. The RF for each compound must meet the criteria in Table 10. For compounds not listed in table, the minimum RF criteria is 0.05.

11.2.10.2.4 When calculating the calibration curve using the linear regression model and 2nd order quadratic, the calibration curve must be evaluated at the lowest concentration calibration standard. The lowest standard is requantitated. The results should be between 70% and 130% recovery of the true value. This low standard evaluation must be kept with the calibration data.

11.2.11 Calibration Check Compounds (CCCs) (8260B only): The CCCs are used to evaluate the validity of the initial calibration. High variability for these compounds may be indicative of system leaks or reactive sites on the column. The percent RSD for each of the CCCs compounds must be less than 30%. The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride.

11.2.12 System Performance Check Compounds (SPCC) (8260B only): The SPCC compounds must be checked before the initial calibration curve is used. Check five compounds (the SPCCs) for a minimum average response factor. These compounds and their respective minimum average RFs are: 1,1-dichloroethane (0.10), bromoform (0.10), chlorobenzene (0.30), chloromethane (0.10) and 1,1,2,2-tetrachloroethane (0.30). If the average RF of any SPCC falls below the minimum RF criteria, then corrective action must be taken before analysis can continue. Possible problems include standard degradation, injection port contamination, contamination at the front end of the column, or active sites in the chromatographic system.

11.2.13 The Initial calibration must be verified analyzing an Initial calibration verification standard (ICV) which is prepared from the second source solutions described in Section 10.2, with a nominal concentration of 20 µg/L. The ICV acceptance criterion is +/- 20%D.

11.3 **Basic Elements of Calibration Review**:

11.3.1 The lowest calibration level must be at or below the RL. If this requirement is not met, the instrument must be recalibrated to include a lower concentration standard. The lowest calibration level must be higher than the MDL.

11.3.2 The minimum number of calibration points requirement must be met. A minimum of five calibration standards is required. For 2nd order quadratic curve a minimum of 6 calibration standards is required. If not, the instrument must be recalibrated.

11.3.3 Linearity requirements as stated in this SOP must be met. If this requirement is not met, the problem must be investigated, fixed and the instrument recalibrated.

11.3.4 Examine the plots for quadratic fits: The calibration plots must be visually examined to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal.

11.3.5 Y-intercept: should be < ½ RL when reporting to the RL and < MDL when reporting to the MDL.

11.3.6 Increasing Response with Increasing Concentration: The instrument signal should increase with every increase in standard concentration.

11.4 **Continuing Calibration Standard (CCAL or CCV)**: Verify the initial calibration curve for each compound of interest once every 12 hours, following BFB calibration and prior to sample analysis. Prepare the CCAL standard (CCV is prepared from the same soruce as the initial calibration standards), then program the Archon or Centurion to add internal and surrogate standard into a 5mL aliquot of the CCAL standard resulting in a final concentration of 30μg/L.

11.4.1 The system software will calculate response factors (RFs) for each compound in the standard.

11.4.2 Percent Deviation (%D) is calculated using the following equation:

$$\%D = \frac{(RF_{CCAL} - Avg\ RF_{ICAL})\ x\ 100}{Avg\ RF_{ICAl}}$$

11.4.3 8260B Continuing Calibration

11.4.3.1 Calibration Check Compounds (CCCs). The CCCs are 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride. If the percent difference for each CCC is ≤ to 20% of the initial calibration it is considered valid. If any CCC fails, the continuing calibration standard may be reanalyzed, however, if all of the compounds of interest are less than or equal to 20% of the initial calibration, the CCAL may still be considered valid. If the problem persists, corrective action must be taken prior to sample analyses (i.e., reprep standards or analyze a new initial calibration curve).

11.4.3.2 System Performance Check Compounds (SPCCs): The SPCCs must meet the same minimum response factor criteria as the ICAL.

11.4.3.3 All other compounds must be less than or equal to 40% of the initial calibration.

11.4.4 8260C Continuing Calibration

11.4.4.1 The %D of all compounds of interest or target analytes must be ≤ 20%. If this criterion is not met, the continuing calibration may still be valid if 80% of the compounds are ≤ 20%D.

11.4.4.2 If a compound that fails the 20% criterion is detected in a sample, the result must be flagged as estimated or the sample must be

reanalyzed with an acceptable continuing calibration that meets the ≤ 20%D crierion. .

11.4.4.3 If the percent difference or percent drift is not ≤ 20% (i.e., > 20%), for more than 20% of the compounds included in the calibration , then corrective action must be taken prior to analysis of samples. Any individual analyte that fails the 20% criterion must have a demonstration of sensitivity in the analytical batch to report non-detects. Detected results may be reported without qualification. The demonstration of sensitivity is the analysis of a low level CCV (LLCCV) at or below the reporting limit. The criterion for passing an LLCCV is detection only and passing an LLCCV allows non-detects to be reported without flagging. The LLCCV is being analyzed immediately after the mid-level CCV.

11.4.4.4 The RF for each compound must meet the criteria in Table 10. For compounds not listed in table 10, the minimum RF criteria is 0.05.

11.5 The concentration used for the continuing calibration standard must be varied from the mid-point concentration at least one time per year.

11.5.1 This standard may be in addition to the typical continuing calibration standard.

11.5.2 The additional standard is to be evaluated against the continuing calibration standard criteria and the results maintained on file.

12. Procedure

12.1 The Archon or Centurion autosampler is used in conjunction with the Tekmar 3000 concentrator and HP GC/MS. For low level soil analysis, the Archon is used in conjunction with the PT^2 in order to link together two Tekmar 3000 concentrators.

12.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

12.3 BFB tuning criteria, GC/MS calibration and/or GC/MS calibration verification criteria must be met before analyzing samples. The samples must be analyzed using the same instrument conditions as those used for the BFB tune and GC/MS calibration.

12.4 Method blank analysis must be performed prior to any sample analysis.

12.4.1 Aqueous samples: For aqueous analysis, the method blank is prepared by filling a 40mL VOA vial with reagent water.

12.4.2 Soils - Low Level: For low level soil analysis, the method blank is prepared by adding 5mL of reagent water and 5g of purified solid matrix to a 40mL VOA vial containing a stir bar.

12.4.3 Soils - Medium Level: For medium level soil analysis, the method blank is prepared by adding 5g of purified solid matrix to 5mL of methanol and extracting for 15 minutes. A 100μL aliquot of the methanol is added to 5mL of reagent water for analysis with aqueous samples.

12.4.4 Waste/oil samples: Prepared the same way as medium level soil samples except 4g of purified solid matrix is added to 10mL of methanol prior to extracting.

12.5 Sample preparation

12.5.1 Aqueous samples: Water samples can be analyzed simply by placing the 40mL VOA vial on the Centurion autosampler. The sample syringe on the Centurion will remove 5mL of sample from the VOA vial. The Centurion is programmed to add internal and surrogate standard into the 5mL aliquot of sample prior to sending the entire 5mL sample to the Tekmar 3000® for purging. The sample is

purged and the VOCs are trapped on the VOCARB 3000. At the conclusion of the purge time, the trap is rapidly heated and backflushed with helium to ensure desorption of the VOCs onto the GC column. After desorption, the GC temperature program separates the compounds before they are sent to the GC/MS for detection. The trap is then baked out and the purging chamber rinsed with reagent water. For information on programming the Centurion, refer to Chapter 3 in the Centurion Operator's Manual. The pH of the sample is taken after sample analysis and is recorded in the instrument logbook.

12.5.1.1 Water Dilutions: If the concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of sample must be diluted and analyzed. Dilutions are made in volumetric flasks and are performed with gastight syringes. Intermediate dilutions may be necessary for extremely high dilutions. Calculate the volume of reagent water to be used and inject the appropriate volume of sample into the reagent water. Cap the flask, and invert three times to mix. This dilution is placed into a 40mL VOA vial and analyzed on the Centurion. Aqueous TCLP extracts are prepared at a 1:10 dilution before analysis.

12.5.2 Soil samples: Soil sample analysis is broken down into low level and medium level analysis. Low level analysis involves heating the sample to 40°C during the purge mode. Medium level analysis is performed diluting an aliquot of methanol extract into 5mL of reagent water and analyzing as a low level soil. Soil samples are collected in either Encore™ samplers, glass jars, or pre-weighed 40mL VOA vials.

12.5.2.1 Low Level Soils: Analysis is performed in a 40mL VOA vial by using approximately 5g of soil in combination with 5mL of organic-free reagent water and a magnetic stir bar. Refer to SOP Method 5035 for sample preparation techniques. The Archon will retrieve the vial and place it in a specially designed soil chamber where the soil is heated to 40°C. The Archon sample syringe then extracts 5mL of reagent water from a clean reservoir, adds internal and surrogate standard to the reagent water, and sends this solution to the 40mL VOA vial containing the sample. The sample is not transferred to the Tekmar 3000 for purging. Purging takes place in the heated soil chamber. After purging, the rest of the sample analysis is identical to that described in the later portion of Section 12.5.1, with the exception that the Archon autosampler is used. Refer to Chapter 5 in the Archon Operator's Manual for information on Archon programming. No pH readings are taken on the soil samples.

12.5.2.2 If the concentration of any target compound in any sample exceeds the initial calibration range, a smaller sample size must be analyzed. If the samples were collected in Encore™ samplers, a medium level analysis must be performed. If the sample was collected in a jar, a smaller aliquot may be analyzed (2.5, 1, 0.5g). In this case, follow the same guidelines as for the 5g analysis. If the sample was collected in a jar and a medium level soil analysis is required. Measure ~5g into a glass scintillation vial, add 5.0mL of methanol and allow the analytes to extract for a minimum of 15 minutes.

12.5.2.3 Medium Level Soils: Medium level soil analysis is based on extracting the soil sample with methanol and adding an aliquot of the methanol extract to reagent water for analysis. This extraction procedure converts the soil into an aqueous sample, thus enabling the soil sample to be analyzed with aqueous samples. Refer to SOP Method

5035 for sample preparation techniques. A 100µL aliquot of the methanol is added to 5mL of reagent water for analysis with low-level soils. The extracted sample (now in a 40mL VOA vial) is analyzed according to the procedure for aqueous samples.

12.5.3 Waste/Oil samples: Refer to Method 5035 for specific preparation techniques. Samples are analyzed under the same conditions as medium level soil samples with the exception of extracting 4g of sample into 10mL of methanol. A minimum of 15 minutes must be allowed for efficient extraction of analytes into the methanol. The same procedure applies to the samples as to the method blank. This rule also applies to TCLP extracts that are insoluble in water.

12.6 Sample Analysis

12.6.1 All samples, blanks, and QC samples must be evaluated according to the criteria listed in Section 14. Any exceptions must be evaluated by the analyst and group leader and documented in the final report.

12.6.2 Once the samples have been analyzed, a detailed quantitation report is generated by the Target® software. This format shows both the raw and subtracted mass spectrum for each compound. The analyst must then determine if the compound matches the standard spectrum or if it is a false identification.

12.6.3 False positives are Q-deleted from the quantitation report so they will not be included in the final report. In the event that the integration performed by the software is not correct, the analyst may perform a manual integration in compliance with the manual integration SOP (S-ALL-Q-016). After analysis, a small amount (~5µL) of sample is removed from the VOA vials to check the pH with wide range pH paper, and the values are included in the instrument run logbook. The pH is only measured for aqueous samples. If the sample has a pH greater than >2, the sample results are flagged and noted in a final report.

12.6.4 Each GC/MS has a logbook, in which all analytical batches for that instrument are recorded, including standards, blanks, and samples. In the computer data system, there are three places where naming conventions are used: sequence ID, data file directory, and the data file name. The Sequence ID is designated by the Instrument ID followed by the two-digit number for the month followed by the day of the month. For example, an analytical sequence on March 17 on instrument MSV3 would be designated as sequence MSV30317. The data file directory is a folder containing the specific data files for that directory (day of analysis). Data file directories are designated by the instrument number followed by the last two digits of the year followed by the two-digit number of the month followed by the day. For example, a directory made for instrument 2 on March 14, 2003 would have the directory designation 2030314. Data file names for samples are named using the instrument ID number, date and three-digit sequential number. For example, the first sample run on MSV1 on March 1 would be 10301001. The sample information associated with the data file consists of the Pace workorder ID, the Pace sample number, dilution and pH. A folder is identified for each sequence/data file directory on each individual instrument. The folder contains hardcopies of BFB tuning report, ICAL or CCAL (depending on what type of calibration was analyzed on that particular date), Method Blank, LCS, MS/MSD, and all samples analyzed during that tune period. These folders are maintained in the Volatiles department in order by date (sequence ID). They are kept in labeled boxes with instrument ID and date ranges. These boxes should not have overlapping years within one box. A new box should be started with each new year.

12.6.5 Raw data files are stored on the network and backed up nightly. Approximately every quarter, the files are transferred to a DVD. The PASI-PGH IT department is responsible for this task. Data are available by copying the files from the DVD back to the network.

13. Calculations

13.1 Qualitative Identification

13.1.1 Target Compounds: The compounds listed in Table 1 shall be identified by an analyst competent in the interpretation of mass spectra. Two criteria must be satisfied to verify the identifications: elution of the sample component at a retention time +/- 30 seconds from the standard component, and correspondence of the sample and standard mass spectra of the continuing calibration.

13.1.2 The guidelines for qualitative verification by comparison of mass spectra are as follows:

13.1.2.1 All characteristic ions should be present. Characteristic ions are defined as the three ions of greatest relative intensity or any ions over 30% relative intensity if fewer than three such ions occur.

13.1.2.2 The relative intensities of the characteristic ions above must agree within 30 percent between the standard and sample spectra.

13.1.2.3 Ions with intensities greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst.

13.1.2.4 These criteria are guidelines. The judgment and experience of the analyst will weigh heavily in the identification of a target analyte.

13.1.3 Non-Target Compounds: A library search may be executed for non-target compounds for the purpose of tentative identification. The provided with the instrument is used for this purpose.

13.1.3.1 Up to 10 organic compounds of greatest concentration that are not a part of the target list for that sample shall be tentatively identified via a search of the mass spectral library. The following are not to be reported: substances with responses less than 10 percent of the internal standard; substances which elute earlier than 30 seconds before the first purgeable target compound, or carbon dioxide. Guidelines for making tentative identification:

13.1.3.1.1 Relative intensities of major ions in the reference spectrum (greater than 10 percent) should be present in the sample spectrum.

13.1.3.1.2 Relative intensities of major ions should agree within 20%.

13.1.3.1.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

13.1.3.1.4 Molecular ions present in the sample spectrum but not in the reference spectrum should be evaluated for possible contamination or co-elution.

13.1.3.1.5 Based on the technical judgment of the analyst and using the data system matching routine as guidance, the compound should be reported as follows:

13.1.3.1.5.1 Report compounds with library matches at or above 90%.

13.1.3.1.5.2 If the library search produces more than one compound at or above 90%, report the first compound.

13.1.3.1.5.3 If no matches were made at or above 90%, the compound should be reported as unknown. If functional groups of compounds are present in the matching criteria, a functional group may be reported instead of just unknown. For example, reporting "unknown ketone" would be more informative than reporting "unknown."

13.2 Concentration Calculations

13.2.1 Target Analytes: Target analytes identified shall be quantified by the internal standard using the equation below:

- Water samples:

$$\text{Concentration } (\mu g/L) = \frac{(Ax)\,(Is)\,(Df)(V_i)}{(Ais)\,(RRF)\,(V_o)}$$

Where:
Ax = Area of primary ion for the compound to be measured
Ais = Area of primary ion for the specific internal standard
Is = Amount of internal standard added in (µg/L)
RRF = Relative response factor from the ICAL, for a specific compound
Df = Dilution factor (The ratio of the number of milliliters purged ,Vo above to the number of mL of the original water sample used for purging.) If no dilution was performed, Df=1.
V_o = Volume of water purged in milliliters (mL)
V_i = Volume of extract injected (mL). For purge and trap analysis, V_i, is not applicable and is set to 1.

Refer to Table 1 for primary ions and internal standards used.

- Low Level Soil Samples:

$$\text{Concentration } (\mu g/Kg) = \frac{(Ax)\,(Is)}{(Ais)\,(RRF)\,(Ws)\,(D)}$$

Where:

Ax = Area of primary ion for the compound to be measured
Ais = Area of primary ion for the specific internal standard
Is = Amount of internal standard added in nanograms (µg/L)
RRF = Relative response factor from the ICAL, for a specific compound
Ws = Weight of sample analyzed in grams (g)
D = (100-%moisture)/100(use only if dry weight is requested)

Refer to Table 1 for primary ions and internal standard used.

- Medium Level Soil Samples:

$$\text{Concentration } (\mu g/Kg) = \frac{(Ax)\,(Is)\,(Vt)\,(1000)\,(Df)}{(Ais)\,(RRF)\,(Ws)\,(D)\,(Va)}$$

Where:
Ax = Area of primary ion for the compound to be measured
Ais = Area of primary ion for the specific internal standard
Is = Amount of internal standard added in nanograms (ng)
RRF = Relative response factor from the ICAL, for a specific compound
Ws = Weight of sample analyzed in grams (g)
D = (100-%moisture)/100 (use only if dry weight is requested)
Vt = Total volume of the methanol extract in milliliters (mL)
Df = Dilution factor The ratio of the number of microliters of methanol added to the reagent water for purging (Va above) to the number of microliters of the methanol extract of the sample contained in that volume Va.
Va = Volume of aliquot taken from methanol extract in microliters (μL)

Please refer to Table 1 for primary ions and internal standard used.

- Matrix Spike/ Matrix Spike Duplicate and LCS

$$\%\ Recovery = \frac{C_{ss} - C_s}{S} \times 100$$

Where:
C_s = Concentration of the source sample
C_{ss} = Concentration of the spiked sample
S = Amount spiked

$$RPD = \frac{|(R_{MS} - R_{MSD}|}{(R_{MS} + R_{MSD})/2} \times 100$$

Where:
R_{MS} = Matrix Spike recovery
R_{MSD} = Matrix Spike Duplicate recovery

13.2.2 Non-target Analytes: An estimated concentration for non-target compounds tentatively identified shall be determined by the nearest internal standard free of interferences. See Table 9 for internal standard references. The calculations are the same as those listed for target compounds with the exception that the RRF is assumed to be 1.0.

14. Quality Control

14.1 With each batch of 20 samples, a method blank (MB), LCS, matrix spike (MS) and matrix spike duplicate (MSD) must be analyzed. The following guidelines apply to the analysis and interpretation of the these:

14.2 Blanks: Method blanks are prepared at a frequency of 5%, that is, one method blank for each group of up to 20 samples analyzed at the same time, by the same procedure in a 12 hour tune period. A volume of clean reference matrix (reagent water for water samples or purified solid matrix for soil/sediment samples) is carried through the entire analytical procedure. The method blank must be analyzed after the calibration. ZHE blanks are prepared and analyzed with TCLP samples. ZHE blanks are to be analyzed with the samples associated with the extraction batch, to verify that the extraction was performed free of contaminants. Instrument blanks may also be analyzed following a sample that exceeded calibration range for any target compounds. An instrument blank is a 5mL aliquot of reagent water analyzed following the same instrument and autosampler pathways as the sample. The results indicate whether sample carryover has occurred.

Any method blank or instrument blank that fails to meet the technical acceptance criteria below must be reanalyzed. Furthermore, all samples including MS/MSD samples, analyzed following an invalid blank must be reanalyzed. If, upon reanalysis, the blank does not meet criteria, the problem must be addressed and noted in the final report. The following acceptance criteria applies to blanks:

14.2.1 The percent recovery of each surrogate standard in the method blank must be within the lab generated acceptance range. See Table 8.

14.2.1.1 If the surrogate recovery is outside the control limits, the blank is not acceptable and must be reanalyzed. All samples associated with an unacceptable blank must be reanalyzed.

14.2.2 The internal standard recovery must be within 50-200% of the internal standards in the most recent continuing calibration standard. See Table 9 for internal standard references.

14.2.3 The retention time shift for each internal standard must be within +/-30 seconds of its retention time in the most recent continuing calibration standard.

14.2.4 The concentration of each target compound found in the blank must be less than the reporting limit or less than one-half the reporting limit listed in Table 1, except for methylene chloride and acetone which must be less than 5 times their reporting limit (RL). For projects requesting detection limits of less than RL listed in Table 1, the blank should be less than one-half the project detection limits, except for methylene chloride and acetone which must be less than 5 times their project detection limit. Results may also be used if a compound is found above the RL in the blank, but less than the RL in all associated samples.

14.2.5 Do NOT subtract the results of the method blank from those of any associated samples.

14.2.6 Method blanks are also used to check for contamination by carryover from a high-concentration sample into subsequent samples. If analytes in the high-concentration sample are NOT found in the subsequent samples, then the lack of carryover has been demonstrated. If there is evidence that carryover may have occurred, then the samples must be reanalyzed. The method blank must be analyzed after the calibration.

14.2.7 When samples that are prepared together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments. A solvent blank should be analyzed on all other instruments on which the set of samples were analyzed to demonstrate that the instrument is not contributing contaminants to the samples.

14.2.8 Corrective actions for handling method blanks that are out of control include checking for carryover, checking for instrument contamination and checking other possible sources of contamination and eliminating or reducing them. Other corrective actions include checking calculations for error, checking the autosampler to ensure proper functioning, and evaluating the effect of the matrix on the test results. If the method blank results do not meet the acceptance criteria above, then the laboratory must take corrective action to locate and reduce the source of the contamination and reprepare and reanalyze any samples associated with the contaminated method blank.

14.3 Laboratory Control Sample (LCS): Include one LCS with each batch of up to 20 samples of the same matrix processed together. Percent recoveries for the LCS must fall within the laboratory-generated acceptance criteria listed in Tables 7 and 8. The CCV is used as the LCS.

14.3.1 A LCS that is determined to be within the criteria effectively establishes that the analytical system is in control and validates system performance for the samples in the associated batch. Samples analyzed along with a LCS determined to be "out of control" shall be considered suspect and the samples must be reprocessed and re-analyzed or the data reported with appropriate data qualifying codes. This includes any allowable marginal exceedance as described below:

14.3.1.1 When the acceptance criteria for the LCS compounds are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes; or

14.3.1.2 When the acceptance criteria for LCS compounds are exceeded low (i.e., low bias), those samples associated with the unacceptable LCS result must be reprepared and reanalyzed along with acceptable LCS.

14.3.1.3 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.4 Spiking compounds are listed in Table 2.

14.4.1 The following criteria shall be used for determining the minimum number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a two (2) year period:

14.4.2 For methods that include one (1) to ten (10) targets, spike all components.

14.4.3 For methods that include eleven (11) to twenty (20) targets, spike at least ten (10) or 80%, whichever is greater.

14.4.4 For methods with more than twenty (20) targets, spike at least sixteen (16) components.

14.5 **Allowable Marginal Exeedances**:

14.5.1 The LCS is spiked with the list of compounds listed in Tables 6 and 7. If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control, therefore corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits are established to determine when corrective action is necessary. A ME is defined as being beyond the LCS control limit (three standard deviations), but within the ME limits. ME limits are between three (3) and four (4) standard deviations around the mean. The number of allowable marginal exceedances is based on the number of analytes in the LCS. **If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary.** This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than eleven analytes.

14.5.2 The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
>90	5
71-90	4
51-70	3
31-50	2

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
11-30	1
<11	0

14.5.3 For method 8260B, greater than 90 compounds are spiked in the LCS, therefore number of marginal exceedances allowed is five. The LCS control limits and the control limits for marginal exceedances are listed in Tables 6 and 7. **If more than 5 analytes exceed the LCS control limits and any one of the five compounds exceeds the marginal exceedance limits, the LCS fails**.

14.5.4 If a LCS is spiked with fewer than 90 compounds, the number of allowed marginal exceedances changes as listed in the table in Section 14.5.2.

14.5.5 If the same analyte exceeds the LCS control limit consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken. A lab track (corrective action database) ticket must be generated describing the failure, root cause and corrective action.

14.6 Matrix Spike/Matrix Spike Duplicates: The laboratory uses these samples to document the effect of matrix on method performance (precision, accuracy and detection limit). Analyze one Matrix Spike/Matrix Spike Duplicate (MS/MSD) pair with each batch of up to 20 samples of the same matrix processed together. The percent recovery acceptance criteria are identical to the LCS recovery limits (see table 6 and table 7) and RPD acceptance criteria is 30%.

14.6.1 Before performing an MS/MSD analysis, analyze the sample used for MS/MSD. Prepare the MS/MSD at the same dilution for which the sample results will be reported. In the event that a sample MS/MSD cannot be analyzed, only a LCS will be reported. MS/MSD samples must meet technical acceptance criteria for internal and surrogate standards, unless the sample, MS and MSD all show similar recovery problems. In this case, all three results are reported and no further analysis is required. However, if the QC criteria fails for either the sample or the MS/MSD, but is acceptable in the other(s), then reanalysis is required.

14.6.2 If matrix spike recoveries are out of control, but the LCS sample results are acceptable, then it can be assumed that the unacceptable MS data are attributable to matrix effects. If MS/MSD recoveries are acceptable, but the RPD is out of control and reanalysis yields similar results, then it can be assumed that the sample matrix is adversely affecting the precision of test.

14.6.3 If the Matrix Spike recoveries do not meet the acceptance criteria, the batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported, and the results noted in the final report.

14.6.4 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.6.5 If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.7 Surrogate Standards: Compare percent recoveries for the surrogates against the laboratory generated acceptance ranges for aqueous and solid matrices.

14.7.1 See Table 8 for surrogate recovery limits.

14.7.2 If the surrogate recoveries are not within limits, then perform the following procedures:

14.7.2.1 Check the standards to ensure proper preparation and that concentration or degradation has not occurred. If problems are found, re-prep standards and reanalyze samples.

14.7.2.2 Check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly.

14.7.2.3 Check instrument performance. If a problem is identified, correct the problem and reanalyze the sample(s).

14.7.2.4 Some samples may contain peaks that interfere with the elution of the surrogate standards (matrix interference). In some instances, sample interferences may be so extreme, that the sample must be diluted in order to achieve adequate quantitation of surrogates and analytes. If sample dilution is required due to matrix effect, documentation of dilution due to matrix must be included in the final report.

14.7.3 If surrogates are below QC limits, reanalysis is required. If, upon reanalysis, the recoveries are again below QC limits, provide both result in project file and place a comment in the final report. If the recoveries are within limits in the reanalysis and the sample was reanalyzed within holding time, report only the reanalysis. If the holding time has expired prior to reanalysis, provide both result in project file, discuss situation with Project Manager, determine reportable data and include the comment in the final report. If surrogate recoveries are above QC limits and the results for the compounds of interest are below the reporting limits, the data may be reported with a comment in the final report.

14.8 Internal Standards: Evaluate the peak area for each internal standard in each analytical sample. The peak areas for the sample internal standards should be >50% and <200% of the respective internal standard peak areas in the most recent calibration verification standard. See Table 9 for internal standard references.

14.8.1 If the internal standard recoveries are not within the above limits, then perform the following procedures:

14.8.1.1 Check the internal standard to ensure proper preparation and that concentration or degradation has not occurred. If problems are found, re-prep standards and reanalyze samples.

14.8.1.2 Check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly.

14.8.1.3 Check instrument performance. If a problem is identified, correct the problem and reanalyze the sample(s).

14.8.1.4 Some samples may contain peaks that interfere with the elution of the internal standards (matrix interference). In some instances, sample interferences may be so extreme that the sample must be diluted in order to achieve adequate quantitation of internals and analytes. If sample dilution is required due to matrix effect, documentation that dilution was performed due to matrix must be included in the final report.

14.8.1.5 If internal standards are above QC limits, reanalysis is required. If, upon reanalysis, the recoveries are below QC limits, provide both runs in project file and include comment in the final report. If the recoveries are within limits in the reanalysis and the sample was reanalyzed within holding time, report only the reanalysis. If the

holding time has expired prior to reanalysis, provide both runs in project file, discuss situation with Project Manager, determine reportable data and include the comment in the final report.

14.9 The initial calibration must meet criteria in order to be valid, otherwise a new ICAL must be analyzed.

14.10 Every 12 hours, or more frequently, a BFB solution must be analyzed. It must meet the tune criteria before any sample analysis can be performed.

14.11 Every 12 hours, or more frequently, a CCAL must be analyzed and must meet the acceptance criteria before any sample analysis can be performed. If the CCAL does not meet the listed criteria, a new ICAL must be analyzed.

14.12 Following the analysis of a CCAL and prior to the analysis of any samples, a method blank must be analyzed and meet acceptance criteria. The method blank must also meet the criteria for surrogate and internal recoveries.

14.13 QC samples must be analyzed with each batch of up to 20 samples of the same matrix. These include LCS, matrix spike and matrix spike duplicates. All QC samples must meet the criteria for surrogate and internal recoveries.

14.14 Samples including method blank, LCS and matrix spikes are analyzed within the 12-hour tune period, as long as all of the above stated criteria are met. Samples must meet the criteria for surrogate and internal recoveries.

14.15 In general, corrective actions include reanalysis of the out-of-control sample to eliminate any isolated problems that may have occurred only on the initial analysis.

14.16 Samples Corrective Action: In all cases, when data are out of control or unacceptable, corrective action must be attempted and reanalysis should be performed, provided that sufficient sample remains to perform reanalysis. If holding times have been exceeded for the initial analysis of a sample, then report the data and include a comment in LIMS that indicates the sample(s) for which the holding time(s) was exceeded. The comment should also indicate that the test results are considered minimum, estimated values. If the holding time has been exceeded for the secondary analysis of a sample (e.g., a dilution, then report as many test results from the initial analysis as possible as well as the test results that required the dilution). Include a comment in the final report that indicates that the sample was initially analyzed within the holding time, but that the subsequent analysis was performed after the holding time has been exceeded. The Project Manager must be notified of any such occurrences and a decision will be made as to what data are reported. Client conditions and contracts may vary so the Project Manager and client must decide what to report.

14.16.1 Surrogates recoveries must be within QC limits listed in Table 8. If surrogate recovery is outside control limits. Reanalyze the sample.

14.16.2 If reanalysis of the out-of-control sample does not yield acceptable data, then the test should be evaluated to determine the possible cause(s). Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis evaluate the usefulness of the data in the final report.

14.17 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.18 If surrogate and internal standard recoveries and responses are out of control and reanalysis yields similar results then perform corrective action to determine the probable cause.

14.18.1 Corrective actions may include: replacing the trap, leak checking the trap, leak checking the GC and the mass spec, retuning the mass spec, cleaning the ion

source of the mass spec, switching filaments the in mass spec that are used for analysis, clipping or replacing the GC column, changing the helium tank, and rinsing of the sample pathway in the purge and trap concentrator to alleviate water problems and/or active sites.

14.19 If method and/or instrument system factors are determined not to be likely causes for the unacceptable data, then the sample matrix is assumed to have an adverse effect on the test results. (Certain matrices such as carbon and clay may absorb organic compounds and prevent their efficient purging, thereby resulting in poor recoveries and responses for surrogates and internal standards. Other matrices such as oils and other organic media, may cause sufficient chromatographic interference as to prevent proper integration of the relevant peaks.) In all cases, the test results should be reported with comments in the final report that indicate the unacceptable results and the probable cause of matrix effects.

14.20 If there is no additional sample available for reanalysis evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 The use of this method is restricted to use by an analyst experienced in the operations of the GC/MS system. The analyst must have read and understood the SOP, as well as the method to which the SOP refers.

15.2 The instrument must meet all the criteria for tuning, calibration, and standardization.

15.3 Acceptable method performance is verified regularly by analysis of performance evaluation samples.

15.4 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.5 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.6 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

16.2 All sample preparation involving the use of organic solvents (methanol, for example) is performed in a fume hood.

16.3 Sample solvent extracts and solvent rinses are collected in appropriate labeled containers.

16.4 After analysis,

16.4.1 Water based soil extracts are disposed of in the trash.

16.4.2 Aqueous samples are discharged into the lab drainage system.

16.4.3 The empty VOA vials that contained aqueous samples are disposed of in glass waste containers. The glass waste containers are then taken to a special dumpster when they are emptied.

16.4.4 Methanol based extracts (waste and soil) and expired standards are poured into a polyethylene flammable waste container. This container is maintained in the volatile department until it is disposed of according to Pace's waste management program.

17. References

17.1 USEPA, Office of Solid Waste and Emergency Response, SW-846, Third Ed., Update III, Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, December 1996.

17.2 USEPA, Office of Solid Waste and Emergency Response, SW-846, Method 8260C, Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 3, August 2006.

17.3 USEPA, Method 5035, Revision 0, December 1996, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples

17.4 USEPA, Method 5035A, Draft Revision 1, July 2002, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples.

17.5 USEPA, Method 5000, Revision 0, December 1996, Sample Preparation for Volatile Organic Compounds.

17.6 USEPA, Method 5030B, Revision 2, December 1996, Purge-and-trap for aqueous samples.

17.7 USEPA, Method 5030C, Revision 3, May 2003, Purge-and-trap for aqueous samples.

17.8 Varian Associates, Archon Purge and Trap AutoSampler System Operator's Manual

17.9 USEPA, SW-846, Third Ed., Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

17.10 USEPA, SW-846, Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

17.11 SOP PGH-O-012, Preparation of EnCore™ Solid Samples by EPA Method 5035A, current version.

17.12 SOP PGH-M-016, Percent Moisture, current version.

17.13 SOP PGH-M-003, TCLP ZHE, current version.

17.14 SOP PGH-M-034, SPLP ZHE, current version.

17.15 SOP PGH-C-026, Control Charts, current version.

17.16 SOP PGH-Q-030, Manual Integrations, current version.

17.17 SOP PGH-C-032, Support Equipment, current version.

17.18 SOP PGH-Q-035, MDL-LOD, current version.

17.19 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.20 SOP PGH-Q-038, Laboratory Equipment, current version.

17.21 SOP PGH-Q-040, Audits, current version

17.22 SOP PGH-Q-039, Corrective Action, current version.

17.23 SOP PGH-Q-044, Monitoring Storage Units, current version.

17.24 SOP S-ALL-Q-020, Training, current version,

17.25 SOP S-ALL-Q-028, Lab Track, current version.

17.26 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.27 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.28 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Table 1 - Characteristic Ions for Volatile Compounds.

18.2 Table 2 - Aqueous Reporting Limits (Current as of date issued).

18.3 Table 3 - Aqueous MDLs (Current as of date issued).

18.4 Table 4 - Solid Reporting Limits (Current as of date issued).

18.5 Table 5 - Solid MDLs (Current as of date issued).

18.6 Table 5A – Medium Level Soil Reporting Limits.

18.7 Table 6 - Aqueous LCS, LCS Marginal Exceedance Limits and Matrix Spike Recovery Limits.

18.8 Table 7 - Solid LCS, LCS Marginal Exceedance Limits and Matrix Spike Recovery Limits.

18.9 Table 8 - Surrogate Recovery Control Limits.

18.10 Table 9 - Internal Standard References.

18.11 Table 10- Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification.

18.12 Appendix No. 1: Internal Standard and Surrogate Loop Calibration Procedure for the Archon Autosampler.

18.13 Appendix No. 2: Surrogate Loop Calibration for the Archon Autosampler.

18.14 Appendix No. 3: Recommended VOC Sample Preservation Techniques and Holding Times.

19. Troubleshooting and Maintenance

19.1 GC/MS quarterly maintenance.

19.1.1 Clean inlet, replace ferrules if necessary.

19.1.2 Dust the outside surface and vacuum the dust out of the electronics area of the instruments.

19.1.3 Clean the source, replace filaments.

19.2 GC/MS Annual maintenance.

19.2.1 Replace oil in the rough pump.

19.2.2 Check the calibration gas vial.

19.2.3 Replace the split vent trap.

19.3 GC/MS Occasional maintenance.

19.3.1 Tune the MS when abundances of internal standards need to be increased or decreased. Or when tune criteria are not met.

19.3.2 Replace the column when peak shape begins to degrade. Prior to replacing the column, it is a good idea to trim up to half a meter from the injector side of the column to see if the column is still usable.

19.4 Autosampler quarterly maintenance

19.4.1 Dust the outside surfaces and vacuum dust from the electronics area of the instrument.

19.5 Autosampler annual maintenance

19.5.1 Replace the transfer lines.

19.5.2 Replace the autosampler needle.

19.5.3 Check the belts, pulleys and bearings.

19.5.4 Clean the rods and screw.

19.6 Concentrator quarterly maintenance.

19.6.1 Clean or replace the sparge vessel.

19.6.2 Dust the outside surface and vacuum dust from the electronics area of the instrument.

19.6.3 Check and adjust the purge gas flow.

19.7 Concentrator occasional maintenance.

19.7.1 Replace the purge trap when peak shape is poor, or when ketones and/or alcohols perform poorly.

19.7.2 Refurbish when samples foam over onto the trap, or when peak shape is poor.

19.8 Computer troubleshooting

19.8.1 Target® Troubleshooting

19.8.1.1 Target® requires Exceed™ to run properly. If Target® is not processing commands properly, shut it down start Exceed™, then start Target®.

19.8.1.2 If Target® is not responding to “Hot Key” commands, make sure the caps lock is turned off.

19.8.2 Chemsation Troubleshooting

19.8.2.1 If sample data are not being acquired, make sure the analytical sequence is not open.

19.8.2.2 If data files do not have any peaks, check that the filament has not burned out. Perform a spectrum scan.

20. Method Modifications

20.1 The method suggests Solid purge temperature of 40ºC, This SOP indicates that solids are at 50ºC.

20.2 The method suggests 5-50ng of BFB for tuning, in the laboratory ~2.5ng is used due to more sensitive instrumentation.

20.3 Method suggests 50µg/L for internal standard and surrogate concentrations. This SOP indicates that 30µg/L is used due to more sensitive instrumentation.

20.4 Purge and trap conditions:

20.4.1 The method suggests 40mL/min; the laboratory purges ~45mL/min.

20.4.2 The method suggests 180ºC desorb temperature; the laboratory desorbs at 245ºC.

20.4.3 The method suggests a desorb time of 4 min; the laboratory desorbs for 0.5min.

20.5 Compounds in marked with an asterisk in table 1 are not listed in 8260C and therefore a method modification.

21. Revisions

Document Number	Reason for Change	Date
PGH-O-15-6	1. Added Method 8260C criteria. 2. Section 8.1.1.3.2-3 removed "pea-sized" and replaced with 6 mm. 3. Section 11.2.10.1.2 added: Performing a linear regression (r ≥ 0.990 or better) or a weighted least squares regression (r ≥ 0.990 or better) must be employed to achieve linearity. A weighted curve is often recommended, unweighted regressions are likely to have high relative errors at the lower concentration levels and are strongly discouraged. Weighted regressions should be used whenever possible. The correlation coefficient r must be ≥ 0.990 or greater when using linear regression. 4. Section 11.2.10.1.3 added: For 2nd order curves such as quadratic the coefficient of determination (COD or r2) r2 ≥ 0.990. 2nd order curves should only be used in circumstances where a linear curve is clearly not appropriate. While quadratic curves are generally reliable within the calibration range, they can produce highly erroneous results above the calibration range including negative numbers at high concentrations. If a quadratic curve is used, each and every calibration plot must be visually inspected to ensure that the fitted function does not re-curve producing multiple concentrations for a single instrument signal. 5. Section 11.2.10.1.4 added when calculating the calibration curve using the linear regression model… 6. Section 11.2.10.2 added 8260C criteria for calibration. See this SOP section for details. 7. Clarified Section 11.4.3 to indicate 8260B continuing calibration. 8. Added Section 11.4.4 8260C continuing calibration. See this SOP section for details. 9. Added Table 10 response factors to used for ICAL and Cont Cal. 10. Added Section 14.4, spiking compounds are listed in Table 2. Also added Sections 14.4.1-14.4.4. 11. Updated references section to add 5030C, 8000C, 8260C, 5035A and Pace Pittsburgh Quality manual.	31July2014
PGH-O-015-7	1. Table 1: added ethanol and tert-amyl ethyl ether. 2. Added note to all applicable Tables regarding compounds not listed in Method 8260C. 3. Added an * to compounds in Tables that are not listed in method 8260C. 4. Edited for spelling and grammar. 5. Reformatted document. 6. Added for method 8260C: When calculating the calibration curve using the linear regression model and 2nd order quadratic, the calibration curve must be evaluated at the lowest concentration calibration standard. The lowest standard is requantitated. The results should be between 70% and 130% recovery of the true value. This low standard evaluation must be kept with the calibration data. 7. Added the requantitation of low standard for linear and quadratic curves for both 8260B and 8260C.	12Jul2014

Document Number	Reason for Change	Date
PGH-O-015-8	1. Section 8.1.3 added reference Appendix 3 – Holding time and preservation requirements for aqueous and solid samples 2. Section 11.3.2 added : A minimum of five calibration standards is required. For 2nd order quadratic curve a minimum of 6 calibration standards is required. 3. Updated SOP references. 4. Added Appendix 3, holding time and preservation requirements. 5. Updated and reorganized section 14 and 15.	15Jun15
PGH-O-015-8	1. Added section 8.2.3: Low level soil samples can be preserved with sodium bisulfate, see Appendix 3 of this SOP. 2. Added section 8.2.4: Medium Level soil samples are preserved with purge ant trap grade methanol. See appendix 3 of this SOP. 3. Added additional surrogate in section 10.8: dibromofluoromethane. Added its ions in Table 1. 4. Added to section 11.4: CCV prepared from the same source as the initial calibration standards. 5. Added dibromofluoromethane surrogate recovery limits in Table 8.	14Aug2015

Table 1
Characteristic Ions for Volatile Compounds (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Compound	Quantitation Ion	Secondary Ions
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	151,153
Ethyl Ether	59	74,54
Acrolein	56	55,58
1,1-Dichloroethene	96	61,63
1,1,2-Trichloro-1,2,2-Trifluoroethane *	101	103,151,153
Acetone	43	58
Iodomethane	142	127,141
Carbon Disulfide	76	78
Acetonitrile	40	41,39
Methyl Acetate *	43	74
Methylene Chloride	84	49,86
TBA, tert-Butyl Alcohol	59	41
Acrylonitrile	53	52,51
trans-1,2-Dichloroethene	96	61,98
Allyl Chloride	76	41,39,81
tert-Butyl Methylether, MTBE	73	57
Vinyl Acetate	43	86
Hexane *	57	43
1,1-Dichloroethane	63	65,83
Chloroprene	88	53,90,51
t-Butyl Ethyl Ether	59	87,57
2,2-Dichloropropane	77	87
cis-1,2-Dichloroethene	96	61,98
2-Butanone	43	72
Propionitrile	54	52,55,40
Ethyl Acetate	43	88,45,61
Diisopropylether	45	43,87
Bromochloromethane	128	49,130
Methacrylonitrile	41	67,39,52,66
Tetrahydrofuran *	42	43,72
Chloroform	83	85,
1.1.1-Trichloroethane	97	99,61
Cyclohexane	56	84,69
Carbon Tetrachloride	117	119
1,1-Dichloropropene	75	77,110

Compound	Quantitation Ion	Secondary Ions
Benzene	78	
1,2-Dichloroethane	62	64,98
Isobutanol	41	56
t-Amyl Methyl Ether	73	43,55,87
Trichloroethene	95	97,130,132
Methylcyclohexane	83	55,98
1,2-Dichloropropane	63	112
Dibromomethane	93	95,174
Methyl methacrylate	41	69,100,39
1,4-Dioxane	88	58
Bromodichloromethane	83	85,127
2-Nitropropane	43	46
2-Chloroethylvinyl Ether	63	65,106
cis-1,3-Dichloropropene	75	77,39
4-Methyl-2-pentanone	43	100,58,85
Toluene	91	92
trans-1,3-Dichloropropene	75	77,39
Ethyl methacrylate	69	41,99,86,114
1,1,2-Trichloroethane	97	83,85
Tetrachloroethene	166	164,129,131
1,3-Dichloropropane	76	78
2-Hexanone	43	58,57,100
Dibromochloromethane	129	208,206
1,2-Dibromoethane, EDB	107	109
Chlorobenzene	112	114,77
1,1,1,2-Tetrachloroethane	131	133,119
Ethylbenzene	106	91
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78
Bromoform	173	171,175,254
Cyclohexanone *	55	98,42,69
n-Propylbenzene	91	120
2-Chlorotouene	126	91
1,3,5-Trimethylbenzene	105	120
Isopropylbenzene, Cumene	105	120
Bromobenzene	158	156,77
1,1,2,2-Tetrachloroethane	83	85,131
1,2,3-Trichloropropane	75	77,
trans-1,4-Dichloro-2-butene	53	88,75
4-Chlorotoluene	91	126
tert-Butylbenzene	91	119,134
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134

Compound	Quantitation Ion	Secondary Ions
1,3-Dichlorobenzene	146	148,111
4-Isopropyltoluene	119	134,91
1,4-Dichlorobenzene	146	148,111
1,2-Dichlorobenzene	146	148,111
n-Butylbenzene	91	92,134
Bis(2-Chloro-1-methyl ethyl) Ether	45	123,121,77
1,2-Dibromo-3-chloropropane	75	155,157
1,2,4-Trichlorobenzne	180	182,145
Hexachlorobutadiene	225	227,223
Naphthalene	128	
1,2,3-Trichlorobenzene	180	182,145
Ethanol	45	46
Tert-Amyl Ethyl Ether		
Internal/Surrogate		
Fluorobenzene	96	77,50
Chlorobenzene-d5	117	119
1,4-Dichlorobenzene-d4	152	150,115
1,4-Dichloroethane-d4	65	10
Toluene-d8	98	100
Bromofluorobenzene	95	174,176
Dibromofluoromethane	111	113,192,190

Table 2
Aqueous Reporting Limits (Current as of date issued) (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Analyte	CAS Number	Reporting Limit	Units
Acetone	67-64-1	10	µg/L
Benzene	71-43-2	1	µg/L
Bromobenzene	108-86-1	1	µg/L
Bromochloromethane	74-97-5	1	µg/L
Bromodichloromethane	75-27-4	1	µg/L
Bromoform	75-25-2	1	µg/L
Bromomethane	74-83-9	1	µg/L
2-Butanone (MEK)	78-93-3	10	µg/L
n-Butylbenzene	104-51-8	1	µg/L
sec-Butylbenzene	135-98-8	1	µg/L
tert-Butylbenzene	98-06-6	1	µg/L
tert-Butyl Alcohol	75-65-0	5	µg/L
Carbon Disulfide	75-15-0	1	µg/L
Carbon tetrachloride	56-23-5	1	µg/L
Chlorobenzene	108-90-7	1	µg/L
Chloroethane	75-00-3	1	µg/L
Chloroform	67-66-3	1	µg/L
Chloromethane	74-87-3	1	µg/L
2-Chlorotoluene	95-49-8	1	µg/L
4-Chlorotoluene	106-43-4	1	µg/L
1,2-Dibromo-3-chloropropane	96-12-8	5	µg/L
Dibromochloromethane	124-48-1	1	µg/L
1,2-Dibromoethane (EDB)	106-93-4	1	µg/L
Dibromomethane	74-95-3	1	µg/L
1,2-Dichlorobenzene	95-50-1	1	µg/L
1,3-Dichlorobenzene	541-73-1	1	µg/L
1,4-Dichlorobenzene	106-46-7	1	µg/L
Dichlorodifluoromethane	75-71-8	1	µg/L
1,1-Dichloroethane	75-34-3	1	µg/L
1,2-Dichloroethane	107-06-2	1	µg/L

Analyte	CAS Number	Reporting Limit	Units
1,2-Dichloroethene (Total)	540-59-0	2	µg/L
1,1-Dichloroethene	75-35-4	1	µg/L
cis-1,2-Dichloroethene	156-59-2	1	µg/L
trans-1,2-Dichloroethene	156-60-5	1	µg/L
1,2-Dichloropropane	78-87-5	1	µg/L
1,3-Dichloropropane	142-28-9	1	µg/L
2,2-Dichloropropane	594-20-7	1	µg/L
1,1-Dichloropropene	563-58-6	1	µg/L
cis-1,3-Dichloropropene	10061-01-5	1	µg/L
trans-1,3-Dichloropropene	10061-02-6	1	µg/L
Ethylbenzene	100-41-4	1	µg/L
Hexachloro-1,3-butadiene	87-68-3	1	µg/L
2-Hexanone	591-78-6	10	µg/L
Isopropylbenzene (Cumene)	98-82-8	1	µg/L
p-Isopropyltoluene	99-87-6	1	µg/L
Methylene Chloride	75-09-2	1	µg/L
4-Methyl-2-pentanone (MIBK)	108-10-1	10	µg/L
Methyl-tert-butyl Ether	1634-04-4	1	µg/L
Naphthalene	91-20-3	2	µg/L
n-Propylbenzene	103-65-1	1	µg/L
Styrene	100-42-5	1	µg/L
1,1,1,2-Tetrachloroethane	630-20-6	1	µg/L
1,1,2,2-Tetrachloroethane	79-34-5	1	µg/L
Tetrachloroethene	127-18-4	1	µg/L
Toluene	108-88-3	1	µg/L
1,2,3-Trichlorobenzene	87-61-6	2	µg/L
1,1,1-Trichloroethane	71-55-6	1	µg/L
1,1,2-Trichloroethane	79-00-5	1	µg/L
Trichloroethene	79-01-6	1	µg/L
Trichlorofluoromethane	75-69-4	1	µg/L
1,2,3-Trichloropropane	96-18-4	1	µg/L
1,2,4-Trimethylbenzene	95-63-6	1	µg/L
1,3,5-Trimethylbenzene	108-67-8	1	µg/L
Vinyl Chloride	75-01-4	1	µg/L
Xylene (Total)	1330-20-7	3	µg/L
M,P-Xylene	179601-23-1	2	µg/L
o-Xylene	95-47-6	1	µg/L
1,1,2-Trichlorotrifluoroethane *	76-13-1	50	µg/L
1,4-Dioxane (p-Dioxane)	123-91-1	100	µg/L
Vinyl Acetate	108-05-4	10	µg/L
Acrylonitrile	107-13-1	2	µg/L

Analyte	CAS Number	Reporting Limit	Units
Iodomethane	74-88-4	50	µg/L
2-Chloroethylvinyl Ether	110-75-8	2	µg/L
trans-1,4-Dichloro-2-butene	110-57-6	5	µg/L
tert-Amylmethyl Ether	994-05-8	1	µg/L
Ethyl-tert-butyl Ether	637-92-3	1	µg/L
Acetonitrile	75-05-8	50	µg/L
TOTAL BTEX		6	µg/L
Methyl Acetate *	79-20-9	5	µg/L
Methylcyclohexane	108-87-2	10	µg/L
n-Hexane *	110-54-3	10	µg/L
Acrolein	107-02-8	2	µg/L
Allyl Chloride	107-05-1	50	µg/L
Diethyl Ether (Ethyl Ether)	60-29-7	1	µg/L
Tetrahydrofuran *	109-99-9	5	µg/L
Methyl methacrylate	80-62-6	1	µg/L
Cyclohexane	110-82-7	10	µg/L
2-Methylnaphthalene *	91-57-6	5	µg/L
Ethyl methacrylate	97-63-2	1	µg/L
Isobutanol	78-83-1	50	µg/L
Propionitrile	107-12-0	5	µg/L
Chloroprene	126-99-8	1	µg/L
Diisopropyl Ether	108-20-3	1	µg/L
Ethanol	64-17-5	200	µg/L
Methacrylonitrile	126-98-7	5	µg/L
Cyclohexanone *	108-94-1	50	µg/L
1,2,4-Trichlorobenzene	120-82-1	1	µg/L

Table 3
Aqueous MDLs (Current as of date issued) (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Analyte	CAS Number	MDL	Units
Acetone	67-64-1	2.62	µg/L
Benzene	71-43-2	0.0647	µg/L
Bromobenzene	108-86-1	0.228	µg/L
Bromochloromethane	74-97-5	0.224	µg/L
Bromodichloromethane	75-27-4	0.149	µg/L
Bromoform	75-25-2	0.254	µg/L
Bromomethane	74-83-9	0.372	µg/L
2-Butanone (MEK)	78-93-3	1.12	µg/L
n-Butylbenzene	104-51-8	0.155	µg/L
sec-Butylbenzene	135-98-8	0.163	µg/L
tert-Butylbenzene	98-06-6	0.284	µg/L
tert-Butyl Alcohol	75-65-0	4.55	µg/L
Carbon Disulfide	75-15-0	0.178	µg/L
Carbon tetrachloride	56-23-5	0.244	µg/L
Chlorobenzene	108-90-7	0.124	µg/L
Chloroethane	75-00-3	0.484	µg/L
Chloroform	67-66-3	0.165	µg/L
Chloromethane	74-87-3	0.209	µg/L
2-Chlorotoluene	95-49-8	0.179	µg/L
4-Chlorotoluene	106-43-4	0.21	µg/L
1,2-Dibromo-3-chloropropane	96-12-8	0.738	µg/L
Dibromochloromethane	124-48-1	0.225	µg/L
1,2-Dibromoethane (EDB)	106-93-4	0.173	µg/L
Dibromomethane	74-95-3	0.194	µg/L
1,2-Dichlorobenzene	95-50-1	0.228	µg/L
1,3-Dichlorobenzene	541-73-1	0.261	µg/L
1,4-Dichlorobenzene	106-46-7	0.17	µg/L
Dichlorodifluoromethane	75-71-8	0.201	µg/L
1,1-Dichloroethane	75-34-3	0.165	µg/L
1,2-Dichloroethane	107-06-2	0.144	µg/L
1,2-Dichloroethene (Total)	540-59-0	0.379	µg/L

Analyte	CAS Number	MDL	Units
1,1-Dichloroethene	75-35-4	0.145	µg/L
cis-1,2-Dichloroethene	156-59-2	0.2	µg/L
trans-1,2-Dichloroethene	156-60-5	0.179	µg/L
1,2-Dichloropropane	78-87-5	0.233	µg/L
1,3-Dichloropropane	142-28-9	0.236	µg/L
2,2-Dichloropropane	594-20-7	0.265	µg/L
1,1-Dichloropropene	563-58-6	0.288	µg/L
cis-1,3-Dichloropropene	10061-01-5	0.186	µg/L
trans-1,3-Dichloropropene	10061-02-6	0.229	µg/L
Ethylbenzene	100-41-4	0.116	µg/L
Hexachloro-1,3-butadiene	87-68-3	0.914	µg/L
2-Hexanone	591-78-6	0.336	µg/L
Isopropylbenzene (Cumene)	98-82-8	0.119	µg/L
p-Isopropyltoluene	99-87-6	0.142	µg/L
Methylene Chloride	75-09-2	0.228	µg/L
4-Methyl-2-pentanone (MIBK)	108-10-1	0.293	µg/L
Methyl-tert-butyl Ether	1634-04-4	0.186	µg/L
Naphthalene	91-20-3	0.327	µg/L
n-Propylbenzene	103-65-1	0.128	µg/L
Styrene	100-42-5	0.175	µg/L
1,1,1,2-Tetrachloroethane	630-20-6	0.141	µg/L
1,1,2,2-Tetrachloroethane	79-34-5	0.224	µg/L
Tetrachloroethene	127-18-4	0.122	µg/L
Toluene	108-88-3	0.108	µg/L
1,2,3-Trichlorobenzene	87-61-6	0.291	µg/L
1,1,1-Trichloroethane	71-55-6	0.191	µg/L
1,1,2-Trichloroethane	79-00-5	0.234	µg/L
Trichloroethene	79-01-6	0.151	µg/L
Trichlorofluoromethane	75-69-4	0.192	µg/L
1,2,3-Trichloropropane	96-18-4	0.343	µg/L
1,2,4-Trimethylbenzene	95-63-6	0.133	µg/L
1,3,5-Trimethylbenzene	108-67-8	0.124	µg/L
Vinyl Chloride	75-01-4	0.126	µg/L
Xylene (Total)	1330-20-7	0.311	µg/L
M,P-Xylene	179601-23-1	0.208	µg/L
o-Xylene	95-47-6	0.104	µg/L
1,1,2-Trichlorotrifluoroethane *	76-13-1	0.14	µg/L
1,4-Dioxane (p-Dioxane)	123-91-1	31.3	µg/L
Vinyl Acetate	108-05-4	1.1	µg/L
Acrylonitrile	107-13-1	1.56	µg/L
Iodomethane	74-88-4	0.671	µg/L
2-Chloroethylvinyl Ether	110-75-8	1.98	µg/L

Analyte	CAS Number	MDL	Units
trans-1,4-Dichloro-2-butene	110-57-6	0.981	µg/L
tert-Amylmethyl Ether	994-05-8	0.2	µg/L
Ethyl-tert-butyl Ether	637-92-3	0.154	µg/L
Acetonitrile	75-05-8	4.3	µg/L
TOTAL BTEX		0.6	µg/L
Methyl Acetate *	79-20-9	1.96	µg/L
Methylcyclohexane	108-87-2	0.242	µg/L
n-Hexane *	110-54-3	0.956	µg/L
Acrolein	107-02-8	1.68	µg/L
Allyl Chloride	107-05-1	2.56	µg/L
Diethyl Ether (Ethyl Ether)	60-29-7	0.341	µg/L
Tetrahydrofuran *	109-99-9	3.12	µg/L
Methyl methacrylate	80-62-6	0.285	µg/L
Cyclohexane	110-82-7	0.24	µg/L
2-Methylnaphthalene *	91-57-6	1.09	µg/L
Ethyl methacrylate	97-63-2	0.429	µg/L
Isobutanol	78-83-1	19.2	µg/L
Propionitrile	107-12-0	1.59	µg/L
Chloroprene	126-99-8	0.147	µg/L
Diisopropyl Ether	108-20-3	0.135	µg/L
Ethanol	64-17-5	36.7	µg/L
Methacrylonitrile	126-98-7	1.08	µg/L
Cyclohexanone *	108-94-1	4.7	µg/L
2,2'-Oxybis(1-chloropropane)	108-60-1	0.585	µg/L
1,2,4-Trichlorobenzene	120-82-1	0.333	µg/L
Preservation pH		1	µg/L

Note: All MDLs values are subject to change, the most current values are in LIMs.

Table 4
Solid Reporting Limits (Current as of date issued) (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Analyte	CAS Number	Reporting Limit	Units
Dichlorodifluoromethane	75-71-8	5	µg/Kg
Chloromethane	74-87-3	5	µg/Kg
Vinyl Chloride	75-01-4	5	µg/Kg
Bromomethane	74-83-9	5	µg/Kg
Chloroethane	75-00-3	5	µg/Kg
Trichlorofluoromethane	75-69-4	5	µg/Kg
Methylene Chloride	75-09-2	5	µg/Kg
1,1-Dichloroethene	75-35-4	5	µg/Kg
trans-1,2-Dichloroethene	156-60-5	5	µg/Kg
1,1-Dichloroethane	75-34-3	5	µg/Kg
tert-Butyl Alcohol	75-65-0	50	µg/Kg
2,2-Dichloropropane	594-20-7	5	µg/Kg
cis-1,2-Dichloroethene	156-59-2	5	µg/Kg
Chloroform	67-66-3	5	µg/Kg
Bromochloromethane	74-97-5	5	µg/Kg
1,1,1-Trichloroethane	71-55-6	5	µg/Kg
Carbon tetrachloride	56-23-5	5	µg/Kg
1,1-Dichloropropene	563-58-6	5	µg/Kg
Benzene	71-43-2	5	µg/Kg
1,2-Dichloroethane	107-06-2	5	µg/Kg
Trichloroethene	79-01-6	5	µg/Kg
1,2-Dichloropropane	78-87-5	5	µg/Kg
Bromodichloromethane	75-27-4	5	µg/Kg
Dibromomethane	74-95-3	5	µg/Kg
trans-1,3-Dichloropropene	10061-02-6	5	µg/Kg
Toluene	108-88-3	5	µg/Kg
cis-1,3-Dichloropropene	10061-01-5	5	µg/Kg
1,1,2-Trichloroethane	79-00-5	5	µg/Kg
Tetrachloroethene	127-18-4	5	µg/Kg
1,3-Dichloropropane	142-28-9	5	µg/Kg

Analyte	CAS Number	Reporting Limit	Units
Dibromochloromethane	124-48-1	5	µg/Kg
1,2-Dibromoethane (EDB)	106-93-4	5	µg/Kg
Chlorobenzene	108-90-7	5	µg/Kg
1,1,1,2-Tetrachloroethane	630-20-6	5	µg/Kg
Ethylbenzene	100-41-4	5	µg/Kg
M,P-Xylene	179601-23-1	10	µg/Kg
o-Xylene	95-47-6	5	µg/Kg
Xylene (Total)	1330-20-7	15	µg/Kg
Styrene	100-42-5	5	µg/Kg
Bromoform	75-25-2	5	µg/Kg
Isopropylbenzene (Cumene)	98-82-8	5	µg/Kg
1,1,2,2-Tetrachloroethane	79-34-5	5	µg/Kg
Bromobenzene	108-86-1	5	µg/Kg
1,2,3-Trichloropropane	96-18-4	5	µg/Kg
n-Propylbenzene	103-65-1	5	µg/Kg
2-Chlorotoluene	95-49-8	5	µg/Kg
1,3,5-Trimethylbenzene	108-67-8	5	µg/Kg
4-Chlorotoluene	106-43-4	5	µg/Kg
tert-Butylbenzene	98-06-6	5	µg/Kg
1,2,4-Trimethylbenzene	95-63-6	5	µg/Kg
sec-Butylbenzene	135-98-8	5	µg/Kg
p-Isopropyltoluene	99-87-6	5	µg/Kg
1,3-Dichlorobenzene	541-73-1	5	µg/Kg
1,4-Dichlorobenzene	106-46-7	5	µg/Kg
n-Butylbenzene	104-51-8	5	µg/Kg
1,2-Dichlorobenzene	95-50-1	5	µg/Kg
1,2-Dibromo-3-chloropropane	96-12-8	5	µg/Kg
1,2,4-Trichlorobenzene	120-82-1	5	µg/Kg
Hexachloro-1,3-butadiene	87-68-3	5	µg/Kg
Naphthalene	91-20-3	5	µg/Kg
1,2,3-Trichlorobenzene	87-61-6	5	µg/Kg
1,4-Dioxane (p-Dioxane)	123-91-1	100	µg/Kg
tert-Amylmethyl Ether	994-05-8	5	µg/Kg
Acetonitrile	75-05-8	50	µg/Kg
Ethyl Acetate	141-78-6	5	µg/Kg
Methyl Acetate *	79-20-9	50	µg/Kg
Methylcyclohexane	108-87-2	10	µg/Kg
n-Hexane *	110-54-3	10	µg/Kg
Methyl methacrylate	80-62-6	5	µg/Kg
Ethyl methacrylate	97-63-2	5	µg/Kg
Isobutanol	78-83-1	50	µg/Kg

Analyte	CAS Number	Reporting Limit	Units
Propionitrile	107-12-0	5	µg/Kg
Chloroprene	126-99-8	5	µg/Kg
Diisopropyl Ether	108-20-3	5	µg/Kg
Methacrylonitrile	126-98-7	5	µg/Kg
1,2-Dichloroethene (Total)	540-59-0	10	µg/Kg
2-Butanone (MEK)	78-93-3	10	µg/Kg
2-Chloroethylvinyl Ether	110-75-8	10	µg/Kg
2-Hexanone	591-78-6	10	µg/Kg
2-Methylnaphthalene *	91-57-6	5	µg/Kg
Allyl Chloride	107-05-1	50	µg/Kg
Carbon Disulfide	75-15-0	5	µg/Kg
Acetone	67-64-1	10	µg/Kg
Acrolein	107-02-8	50	µg/Kg
Acrylonitrile	107-13-1	5	µg/Kg
Cyclohexane	110-82-7	10	µg/Kg
Diethyl Ether (Ethyl Ether)	60-29-7	5	µg/Kg
Iodomethane	74-88-4	50	µg/Kg
Methyl-tert-butyl Ether	1634-04-4	5	µg/Kg
4-Methyl-2-pentanone (MIBK)	108-10-1	10	µg/Kg
trans-1,4-Dichloro-2-butene	110-57-6	5	µg/Kg
Tetrahydrofuran *	109-99-9	5	µg/Kg
1,1,2-Trichlorotrifluoroethane *	76-13-1	50	µg/Kg
Vinyl Acetate	108-05-4	50	µg/Kg
TOTAL BTEX		30	µg/Kg
Cyclohexanone *	108-94-1	50	µg/Kg
Ethyl-tert-butyl Ether	637-92-3	5	µg/Kg
Hexane		10	µg/Kg
2-Nitropropane	79-46-9	50	µg/Kg
Ethanol	64-17-5	200	µg/Kg

Table 5
Solid MDLs (Current as of date issued) (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Analyte	CAS Number	MDL	Units
Dichlorodifluoromethane	75-71-8	0.89	µg/Kg
Chloromethane	74-87-3	1.05	µg/Kg
Vinyl Chloride	75-01-4	0.808	µg/Kg
Bromomethane	74-83-9	2.94	µg/Kg
Chloroethane	75-00-3	1.63	µg/Kg
Trichlorofluoromethane	75-69-4	0.89	µg/Kg
Methylene Chloride	75-09-2	1.34	µg/Kg
1,1-Dichloroethene	75-35-4	0.811	µg/Kg
trans-1,2-Dichloroethene	156-60-5	0.819	µg/Kg
1,1-Dichloroethane	75-34-3	0.793	µg/Kg
tert-Butyl Alcohol	75-65-0	6.93	µg/Kg
2,2-Dichloropropane	594-20-7	0.803	µg/Kg
cis-1,2-Dichloroethene	156-59-2	2.46	µg/Kg
Chloroform	67-66-3	0.711	µg/Kg
Bromochloromethane	74-97-5	0.776	µg/Kg
1,1,1-Trichloroethane	71-55-6	2.6	µg/Kg
Carbon tetrachloride	56-23-5	0.89	µg/Kg
1,1-Dichloropropene	563-58-6	0.631	µg/Kg
Benzene	71-43-2	0.78	µg/Kg
1,2-Dichloroethane	107-06-2	0.91	µg/Kg
Trichloroethene	79-01-6	0.756	µg/Kg
1,2-Dichloropropane	78-87-5	1.62	µg/Kg
Bromodichloromethane	75-27-4	1.81	µg/Kg
Dibromomethane	74-95-3	2.47	µg/Kg
trans-1,3-Dichloropropene	10061-02-6	1.63	µg/Kg
Toluene	108-88-3	0.643	µg/Kg
cis-1,3-Dichloropropene	10061-01-5	1.57	µg/Kg
1,1,2-Trichloroethane	79-00-5	0.921	µg/Kg
Tetrachloroethene	127-18-4	0.726	µg/Kg
1,3-Dichloropropane	142-28-9	0.771	µg/Kg
Dibromochloromethane	124-48-1	1.53	µg/Kg

Analyte	CAS Number	MDL	Units
1,2-Dibromoethane (EDB)	106-93-4	2.61	µg/Kg
Chlorobenzene	108-90-7	0.991	µg/Kg
1,1,1,2-Tetrachloroethane	630-20-6	0.965	µg/Kg
Ethylbenzene	100-41-4	2.57	µg/Kg
M,P-Xylene	179601-23-1	1.93	µg/Kg
o-Xylene	95-47-6	1.13	µg/Kg
Xylene (Total)	1330-20-7	3.06	µg/Kg
Styrene	100-42-5	1.11	µg/Kg
Bromoform	75-25-2	2.53	µg/Kg
Isopropylbenzene (Cumene)	98-82-8	1.06	µg/Kg
1,1,2,2-Tetrachloroethane	79-34-5	0.887	µg/Kg
Bromobenzene	108-86-1	1.05	µg/Kg
1,2,3-Trichloropropane	96-18-4	1.03	µg/Kg
n-Propylbenzene	103-65-1	1.29	µg/Kg
2-Chlorotoluene	95-49-8	1.12	µg/Kg
1,3,5-Trimethylbenzene	108-67-8	1.35	µg/Kg
4-Chlorotoluene	106-43-4	1.09	µg/Kg
tert-Butylbenzene	98-06-6	1.97	µg/Kg
1,2,4-Trimethylbenzene	95-63-6	1.16	µg/Kg
sec-Butylbenzene	135-98-8	1.46	µg/Kg
p-Isopropyltoluene	99-87-6	2.06	µg/Kg
1,3-Dichlorobenzene	541-73-1	1.27	µg/Kg
1,4-Dichlorobenzene	106-46-7	1.22	µg/Kg
n-Butylbenzene	104-51-8	2.16	µg/Kg
1,2-Dichlorobenzene	95-50-1	1.09	µg/Kg
1,2-Dibromo-3-chloropropane	96-12-8	1.71	µg/Kg
1,2,4-Trichlorobenzene	120-82-1	1.36	µg/Kg
Hexachloro-1,3-butadiene	87-68-3	1.98	µg/Kg
Naphthalene	91-20-3	2.52	µg/Kg
1,2,3-Trichlorobenzene	87-61-6	1.47	µg/Kg
1,4-Dioxane (p-Dioxane)	123-91-1	30.6	µg/Kg
tert-Amylmethyl Ether	994-05-8	0.647	µg/Kg
Acetonitrile	75-05-8	8.98	µg/Kg
Ethyl Acetate	141-78-6	0.957	µg/Kg
Methyl Acetate *	79-20-9	3.02	µg/Kg
Methylcyclohexane	108-87-2	2.33	µg/Kg
n-Hexane *	110-54-3	2.45	µg/Kg
Methyl Methacrylate	80-62-6	1.76	µg/Kg
Ethyl Methacrylate	97-63-2	1.54	µg/Kg
Isobutanol	78-83-1	29.7	µg/Kg
Propionitrile	107-12-0	2.95	µg/Kg
Chloroprene	126-99-8	0.813	µg/Kg

Analyte	CAS Number	MDL	Units
Diisopropyl Ether	108-20-3	0.784	µg/Kg
Ethanol	64-17-5	26.1	µg/Kg
Methacrylonitrile	126-98-7	1.53	µg/Kg
1,2-Dichloroethene (Total)	540-59-0	3.28	µg/Kg
2-Butanone (MEK)	78-93-3	1.26	µg/Kg
2-Chloroethylvinyl Ether	110-75-8	0.52	µg/Kg
2-Hexanone	591-78-6	1.18	µg/Kg
2-Methylnaphthalene *	91-57-6	1.64	µg/Kg
Allyl Chloride	107-05-1	3.82	µg/Kg
Carbon Disulfide	75-15-0	0.767	µg/Kg
Acetone	67-64-1	1.95	µg/Kg
Acrolein	107-02-8	5.39	µg/Kg
Acrylonitrile	107-13-1	3.27	µg/Kg
Cyclohexane	110-82-7	1.25	µg/Kg
Diethyl Ether (Ethyl Ether)	60-29-7	0.876	µg/Kg
Iodomethane	74-88-4	1.07	µg/Kg
Methyl-tert-butyl Ether	1634-04-4	0.711	µg/Kg
4-Methyl-2-pentanone (MIBK)	108-10-1	1.03	µg/Kg
trans-1,4-Dichloro-2-butene	110-57-6	1.26	µg/Kg
Tetrahydrofuran *	109-99-9	1.52	µg/Kg
1,1,2-Trichlorotrifluoroethane *	76-13-1	0.665	µg/Kg
Vinyl Acetate	108-05-4	1.4	µg/Kg
TOTAL BTEX		7.05	µg/Kg
Cyclohexanone *	108-94-1	12.3	µg/Kg
Ethyl-tert-butyl Ether	637-92-3	0.788	µg/Kg
2,2'-Oxybis(1-chloropropane)	108-60-1	0.788	µg/Kg
2-Nitropropane	79-46-9	11.4	µg/Kg

Note: All MDLs values are subject to change, the most current values are in LIMs.

Table 5A
Medium Level Soil Reporting Limits (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Analyte	CAS Number	Reporting Limit	Units
1,1,1,2-Tetrachloroethane	630-20-6	250	µg/Kg
1,1,1-Trichloroethane	71-55-6	250	µg/Kg
1,1,2,2-Tetrachloroethane	79-34-5	250	µg/Kg
1,1,2-Trichloroethane	79-00-5	250	µg/Kg
1,1,2-Trichlorotrifluoroethane *	76-13-1	2500	µg/Kg
1,1-Dichloroethane	75-34-3	250	µg/Kg
1,1-Dichloroethene	75-35-4	250	µg/Kg
1,1-Dichloropropene	563-58-6	250	µg/Kg
1,2,3-Trichlorobenzene	87-61-6	250	µg/Kg
1,2,3-Trichloropropane	96-18-4	250	µg/Kg
1,2,4-Trichlorobenzene	120-82-1	250	µg/Kg
1,2,4-Trimethylbenzene	95-63-6	250	µg/Kg
1,2-Dibromo-3-chloropropane	96-12-8	250	µg/Kg
1,2-Dibromoethane (EDB)	106-93-4	250	µg/Kg
1,2-Dichlorobenzene	95-50-1	250	µg/Kg
1,2-Dichloroethane	107-06-2	250	µg/Kg
1,2-Dichloroethene (Total)	540-59-0	500	µg/Kg
1,2-Dichloropropane	78-87-5	250	µg/Kg
1,3,5-Trimethylbenzene	108-67-8	250	µg/Kg
1,3-Dichlorobenzene	541-73-1	250	µg/Kg
1,3-Dichloropropane	142-28-9	250	µg/Kg
1,4-Dichlorobenzene	106-46-7	250	µg/Kg
1,4-Dioxane (p-Dioxane)	123-91-1	5000	µg/Kg
2,2-Dichloropropane	594-20-7	250	µg/Kg
2-Butanone (MEK)	78-93-3	500	µg/Kg
2-Chlorotoluene	95-49-8	250	µg/Kg
2-Hexanone	591-78-6	500	µg/Kg
2-Methylnaphthalene *	91-57-6	250	µg/Kg
4-Chlorotoluene	106-43-4	250	µg/Kg
4-Methyl-2-pentanone (MIBK)	108-10-1	500	µg/Kg
Acetone	67-64-1	500	µg/Kg
Acetonitrile	75-05-8	2500	µg/Kg
Acrolein	107-02-8	2500	µg/Kg
Acrylonitrile	107-13-1	250	µg/Kg
Allyl Chloride	107-05-1	2500	µg/Kg

Analyte	CAS Number	Reporting Limit	Units
Benzene	71-43-2	250	µg/Kg
Bromobenzene	108-86-1	250	µg/Kg
Bromochloromethane	74-97-5	250	µg/Kg
Bromodichloromethane	75-27-4	250	µg/Kg
Bromoform	75-25-2	250	µg/Kg
Bromomethane	74-83-9	250	µg/Kg
Carbon Disulfide	75-15-0	250	µg/Kg
Carbon tetrachloride	56-23-5	250	µg/Kg
Chlorobenzene	108-90-7	250	µg/Kg
Chloroethane	75-00-3	250	µg/Kg
Chloroform	67-66-3	250	µg/Kg
Chloromethane	74-87-3	250	µg/Kg
Chloroprene	126-99-8	250	µg/Kg
cis-1,2-Dichloroethene	156-59-2	250	µg/Kg
cis-1,3-Dichloropropene	10061-01-5	250	µg/Kg
Cyclohexane	110-82-7	500	µg/Kg
Cyclohexanone *	108-94-1	2500	µg/Kg
Dibromochloromethane	124-48-1	250	µg/Kg
Dibromomethane	74-95-3	250	µg/Kg
Dichlorodifluoromethane	75-71-8	250	µg/Kg
Diethyl Ether (Ethyl Ether)	60-29-7	250	µg/Kg
Diisopropyl Ether	108-20-3	250	µg/Kg
Ethanol	64-17-5	2500	µg/Kg
Ethyl Acetate	141-78-6	250	µg/Kg
Ethyl Methacrylate	97-63-2	250	µg/Kg
Ethylbenzene	100-41-4	250	µg/Kg
Ethyl-tert-butyl Ether	637-92-3	250	µg/Kg
Hexachloro-1,3-butadiene	87-68-3	250	µg/Kg
Iodomethane	74-88-4	2500	µg/Kg
Isobutanol	78-83-1	2500	µg/Kg
Isopropylbenzene (Cumene)	98-82-8	250	µg/Kg
M,P-Xylene	179601-23-1	500	µg/Kg
Methacrylonitrile	126-98-7	250	µg/Kg
Methyl Acetate *	79-20-9	2500	µg/Kg
Methyl Methacrylate	80-62-6	250	µg/Kg
Methylcyclohexane	108-87-2	500	µg/Kg
Methylene Chloride	75-09-2	250	µg/Kg

Analyte	CAS Number	Reporting Limit	Units
Methyl-tert-butyl Ether	1634-04-4	2500	µg/Kg
Naphthalene	91-20-3	250	µg/Kg
n-Butylbenzene	104-51-8	250	µg/Kg
n-Hexane *	110-54-3	500	µg/Kg
n-Propylbenzene	103-65-1	250	µg/Kg
o-Xylene	95-47-6	250	µg/Kg
p-Isopropyltoluene	99-87-6	250	µg/Kg
Propionitrile	107-12-0	250	µg/Kg
sec-Butylbenzene	135-98-8	250	µg/Kg
Styrene	100-42-5	250	µg/Kg
tert-Amylmethyl Ether	994-05-8	250	µg/Kg
tert-Butyl Alcohol	75-65-0	2500	µg/Kg
tert-Butylbenzene	98-06-6	250	µg/Kg
Tetrachloroethene	127-18-4	250	µg/Kg
Tetrahydrofuran *	109-99-9	250	µg/Kg
Toluene	108-88-3	250	µg/Kg
TOTAL BTEX		1500	µg/Kg
trans-1,2-Dichloroethene	156-60-5	250	µg/Kg
trans-1,3-Dichloropropene	10061-02-6	250	µg/Kg
trans-1,4-Dichloro-2-butene	110-57-6	250	µg/Kg
Trichloroethene	79-01-6	250	µg/Kg
Trichlorofluoromethane	75-69-4	250	µg/Kg
Vinyl Acetate	108-05-4	2500	µg/Kg
Vinyl Chloride	75-01-4	250	µg/Kg
Xylene (Total)	1330-20-7	750	µg/Kg

Table 6
Aqueous LCS, LCS Marginal Exceedance Limits and Matrix Spike % Recovery Limits (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Note: Marginal Exceedance limits only apply to LCS.

Parameter	LME	UME	LCL	UCL
1,1,1,2-Tetrachloroethane	55	137	65	127
1,1,1-Trichloroethane	51	142	62	130
1,1,2,2-Tetrachloroethane	67	122	74	115
1,1,2-Trichloroethane	65	129	73	121
1,1,2-Trichlorotrifluoroethane*	16	200	42	196
1,1-Dichloroethane	53	135	64	125
1,1-Dichloroethene	47	137	58	126
1,1-Dichloropropene	58	124	66	116
1,2,3-Trichlorobenzene	52	159	66	146
1,2,3-Trichloropropane	56	130	66	121
1,2,4-Trichlorobenzene	61	147	72	136
1,2,4-Trimethylbenzene	61	132	70	123
1,2-Dibromo-3-chloropropane	45	138	56	126
1,2-Dibromoethane (EDB)	69	120	75	113
1,2-Dichlorobenzene	69	124	76	117
1,2-Dichloroethane	56	133	66	124
1,2-Dichloropropane	57	127	66	119
1,3,5-Trimethylbenzene	58	132	67	123
1,3-Dichlorobenzene	66	123	73	116
1,3-Dichloropropane	69	121	75	115
1,4-Dichlorobenzene	67	126	75	119
1,4-Dioxane	10	200	26	175
2,2-Dichloropropane	19	165	37	146
2-Butanone (MEK)	60	136	69	126
2-Chloroethylvinyl ether	55	132	65	123
2-Chlorotoluene	63	122	70	114
2-Hexanone	42	129	53	118
2-Methylnaphthalene*	10	200	34	175
4-Chlorotoluene	63	123	71	116
4-Methyl-2-pentanone (MIBK)	59	133	68	124
Acetone	42	156	56	142
Acetonitrile	39	166	55	150
Acrylonitrile	41	133	52	121
Allyl Chloride	23	198	45	176
Benzene	60	132	69	123
Bromobenzene	59	127	68	118
Bromochloromethane	49	145	61	133
Bromodichloromethane	54	129	64	120
Bromoform	43	146	56	133
Bromomethane	10	173	19	151
Carbon Disulfide	33	193	53	173

Parameter	LME	UME	LCL	UCL
Carbon Tetrachloride	38	147	52	133
Chlorobenzene	63	130	72	121
Chloroethane	38	158	53	143
Chloroform	53	133	63	123
Chloromethane	33	154	48	139
cis-1,2-Dichloroethene	53	133	63	123
cis-1,3-Dichloropropene	56	130	65	121
Cyclohexane	42	158	57	144
Cyclohexanone*	33	105	42	96
Dibromochloromethane	46	145	58	132
Dibromomethane	61	134	70	125
Dichlorodifluoromethane	10	178	30	157
Diethyl ether (Ethyl Ether)	64	122	71	115
Diisopropyl Ether	55	141	66	131
Ethanol	10	200	11	175
Ethyl methacrylate	33	136	46	123
Ethylbenzene	62	132	70	123
Ethyl-tert-butyl-ether	58	133	67	124
Hexachloro-1,3-Butadiene	57	143	68	132
Iodomethane	10	200	10	175
Isobutanol	31	188	51	168
Isopropylbenzene (Cumene)	55	148	66	136
m,p-Xylene	62	133	71	124
Methacrylonitrile	46	138	57	126
Methyl Acetate*	59	187	75	171
Methyl methacrylate	52	131	62	121
Methylcyclohexane	38	170	54	154
Methylene Chloride	42	147	55	134
Methyl-tert-butyl-ether (MTBE)	58	143	69	133
Naphthalene	53	146	65	134
n-Butylbenzene	61	129	69	120
n-Hexane*	16	181	37	161
n-Propylbenzene	65	123	72	116
o-Xylene	61	127	69	118
p-Isopropyltoluene	69	124	76	117
Propionitrile	57	132	66	123
sec-Butylbenzene	65	124	72	116
Styrene	56	136	66	126
tert-Amylmethyl ether	50	130	60	120
tert-Butyl Alcohol (TBA)	20	180	40	160
tert-Butyl Benzene	65	123	72	116
Tetrachloroethene	51	143	62	131
Tetrahydrofuran*	41	146	54	133
Toluene	65	131	73	123
Total Xylenes	61	131	70	123
trans-1,2-Dichloroethene	51	134	61	124

Parameter	LME	UME	LCL	UCL
trans-1,3-Dichloropropene	63	118	70	111
trans-1,4-Dichloro-2-butene	27	126	40	114
Trichloroethene	56	135	66	125
Trichlorofluoromethane	42	159	57	144
Vinyl acetate	10	76	10	62
Vinyl chloride	46	143	58	131

Note: All control Limits are subject to change, the most current control limits are in the laboratory's LIMs.

Table 7
Solid LCS, LCS Marginal Exeedance Limits and Matrix Spike Recovery Limits (Compounds marked with an * are not listed on method 8260C and are therefore a method modification)

Note: Marginal Exceedance limits only apply to LCS

Parameter	LME	UME	LCL	UCL
1,1,1,2-Tetrachloroethane	50	130	60	120
1,1,1-Trichloroethane	47	136	58	125
1,1,2,2-Tetrachloroethane	35	133	47	121
1,1,2-Trichloroethane	47	127	57	117
1,1,2-Trichlorotrifluoroethane*	21	199	43	177
1,1-Dichloroethane	48	137	59	126
1,1-Dichloroethene	38	157	53	142
1,1-Dichloropropene	37	146	51	132
1,2,3-Trichlorobenzene	28	155	44	139
1,2,3-Trichloropropane	46	132	57	121
1,2,4-Trichlorobenzene	27	163	44	146
1,2,4-Trimethylbenzene	42	144	54	131
1,2-Dibromo-3-chloropropane	11	148	28	131
1,2-Dibromoethane (EDB)	49	119	57	110
1,2-Dichlorobenzene	38	145	51	132
1,2-Dichloroethane	40	132	52	121
1,2-Dichloropropane	47	133	58	122
1,3,5-Trimethylbenzene	41	144	54	131
1,3-Dichlorobenzene	39	143	52	130
1,3-Dichloropropane	49	132	60	121
1,4-Dichlorobenzene	40	143	53	130
1,4-Dioxane	10	161	26	141
2,2-Dichloropropane	13	163	31	144
2-Butanone (MEK)	39	141	52	129
2-Chloroethylvinyl ether	10	200	10	175
2-Chlorotoluene	39	152	53	138
2-Hexanone	33	127	45	116
2-Methylnaphthalene*	10	196	14	170
4-Chlorotoluene	40	151	54	137
4-Methyl-2-pentanone (MIBK)	41	134	52	122
Acetone	10	200	12	183
Acetonitrile	10	168	29	148
Acrylonitrile	45	127	55	117
Allyl Chloride	21	189	42	168
Benzene	40	139	52	126
Bromobenzene	33	151	48	136
Bromochloromethane	55	118	63	110
Bromodichloromethane	38	125	49	114
Bromoform	18	137	33	123
Bromomethane	10	200	12	179
Carbon Disulfide	10	186	31	163

Parameter	LME	UME	LCL	UCL
Carbon Tetrachloride	48	136	59	125
Chlorobenzene	51	132	61	122
Chloroethane	46	165	61	150
Chloroform	47	132	58	121
Chloromethane	30	148	45	133
cis-1,2-Dichloroethene	47	132	57	121
cis-1,3-Dichloropropene	32	132	44	119
Cyclohexane	37	146	50	132
Cyclohexanone*	10	200	10	175
Dibromochloromethane	35	126	46	115
Dibromomethane	50	126	59	116
Dichlorodifluoromethane	10	200	15	184
Diethyl ether (Ethyl Ether)	53	127	62	118
Diisopropyl Ether	46	165	61	150
Ethanol	10	200	10	175
Ethyl methacrylate	10	132	24	117
Ethylbenzene	42	140	54	128
Ethyl-tert-butyl-ether	40	121	50	111
Hexachloro-1,3-Butadiene	10	198	28	174
Iodomethane	10	157	26	138
Isobutanol	21	126	34	113
Isopropylbenzene (Cumene)	44	158	58	144
m,p-Xylene	42	139	54	127
Methyl Acetate*	25	178	44	159
Methyl methacrylate	20	141	35	126
Methylcyclohexane	20	166	38	147
Methylene Chloride	10	174	21	152
Methyl-tert-butyl-ether (MTBE)	44	141	57	129
Naphthalene	17	171	36	152
n-Butylbenzene	21	175	41	156
n-Hexane*	10	200	10	175
n-Propylbenzene	35	160	51	144
o-Xylene	35	145	49	131
p-Isopropyltoluene	28	163	45	146
sec-Butylbenzene	35	161	51	145
Styrene	36	136	48	123
tert-Amylmethyl ether	42	107	50	99
tert-Butyl Alcohol (TBA)	33	139	47	126
tert-Butyl Benzene	40	153	54	139
Tetrachloroethene	49	141	60	129
Tetrahydrofuran*	47	121	57	112
Toluene	40	140	53	127
Total Xylenes	41	139	53	127
trans-1,2-Dichloroethene	41	141	54	129
trans-1,3-Dichloropropene	32	123	43	111
trans-1,4-Dichloro-2-butene	32	102	41	93

Parameter	LME	UME	LCL	UCL
Trichloroethene	46	134	57	123
Trichlorofluoromethane	44	158	58	144
Vinyl acetate	10	0	10	175
Vinyl chloride	36	150	51	135

Table 8
Surrogate %Recovery Control Limits

Analyte	Lower Control Limits(Water)	Upper Control Limits (Water)	Lower Control Limit (Soil)	Upper Control Limit (Soil)
1,2-Dichloroethane-d4	84	124	83	138
4-Bromofluorobenzene	84	113	71	124
Toluene-d8	79	118	73	124
Dibromofluoromethane	70	130	70	130

Note: All control Limits are subject to change, the most current control limits are in the laboratory's LIMs.

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Table 9
Internal Standard References

Analyte	Internal Standard Reference
1,1,1,2-Tetrachloroethane	2
1,1,1-Trichloroethane	1
1,1,2,2-Tetrachloroethane	3
1,1,2-Trichloroethane	2
1,1,2-Trichlorotrifluoroethane	1
1,1-Dichloroethane	1
1,1-Dichloroethene	1
1,1-Dichloropropene	1
1,2,3-Trichlorobenzene	3
1,2,3-Trichloropropane	3
1,2,4-Trichlorobenzene	3
1,2,4-Trimethylbenzene	3
1,2-Dibromo-3-chloropropane	3
1,2-Dibromoethane (EDB)	2
1,2-Dichlorobenzene	3
1,2-Dichloroethane	1
1,2-Dichloropropane	2
1,3,5-Trimethylbenzene	3
1,3-Dichlorobenzene	3
1,3-Dichloropropane	3
1,4-Dichlorobenzene	3
1,4-Dioxane (p-Dioxane)	2
2,2-Dichloropropane	1
2-Butanone (MEK)	1
2-Chlorotoluene	3
2-Hexanone	2
2-Methylnaphthalene	3
4-Chlorotoluene	3
4-Methyl-2-pentanone (MIBK)	2
Acetone	1
Benzene	2
Bromobenzene	3
Bromochloromethane	1
Bromodichloromethane	2
Bromoform	3
Bromomethane	1
Carbon Disulfide	1
Carbon tetrachloride	1

Analyte	Internal Standard Reference
Chlorobenzene	2
Chloroethane	1
Chloroform	1
Chloromethane	1
Cyclohexane	1
Dibromochloromethane	2
Dibromomethane	2
Dichlorodifluoromethane	2
Diisopropyl Ether	1
Ethanol	3
Ethyl-tert-butyl Ether	1
Ethylbenzene	2
Hexachloro-1,3-butadiene	3
Isopropylbenzene (Cumene)	3
Methyl Acetate	1
Methyl-tert-butyl Ether	1
Methylcyclohexane	1
Methylene Chloride	1
Naphthalene	3
Styrene	3
Tetrachloroethene	2
Toluene	2
Trichloroethene	2
Trichlorofluoromethane	1
Vinyl Acetate	1
Vinyl Chloride	1
cis-1,2-Dichloroethene	1
cis-1,3-Dichloropropene	2
M,P-Xylene	2
n-Butylbenzene	3
n-Propylbenzene	3
o-Xylene	2
p-Isopropyltoluene	3
sec-Butylbenzene	3
tert-Amylmethyl Ether	2
tert-Butyl Alcohol	1
tert-Butylbenzene	3
trans-1,2-Dichloroethene	1
trans-1,3-Dichloropropene	2

Table 10
Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification
(for method 8260C)

Volatile Compounds	Minimum Response Factor (RF)[a]	Typical Response Factor (RF)[b]
Dichlorodifluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.100	0.255
Chloroethane	0.100	0.254
Trichlorofluoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100	0.302
Acetone	0.100	0.151
Carbon disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2-Dichloroethene	0.100	0.351
cis-1,2-Dichloroethene	0.100	0.376
Methyl tert-Butyl Ether	0.100	0.847
1,1-Dichloroethane	0.200	0.655
2-Butanone	0.100	0.216
Chloroform	0.200	0.557
1,1,1-Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon tetrachloride	0.100	0.353
Benzene	0.500	1.368
1,2-Dichloroethane	0.100	0.443
Trichloroethene	0.200	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382

Table 10
Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification (Cont.)

Volatile Compounds	Minimum Response Factor (RF)[a]	Typical Response Factor (RF)[b]
Bromodichloromethane	0.200	0.424
cis-1,3-Dichloropropene	0.200	0.537
trans-1,3-Dichloropropene	0.100	0.515
4-Methyl-2-pentanone	0.100	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518
Tetrachloroethene	0.200	0.606
2-Hexanone	0.100	0.536
Dibromochloromethane	0.100	0.652
1,2-Dibromoethane	0.100	0.634
Chlorobenzene	0.500	1.733
Ethylbenzene	0.100	2.827
meta-/para-Xylene	0.100	1.080
ortho-Xylene	0.300	1.073
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo-3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806

[a] The project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed. In addition, lower than the recommended minimum response factors may be acceptable for those compounds that are not considered critical target analytes and the associated data may be used for screening purposes.
[b] Data provided by EPA Region III laboratory.

Appendix No. 1 - Internal Standard and Surrogate Loop Calibration Procedure for the Archon Autosampler

2.13 Calibration of the Sample Vial Gripper

After the Archon is installed to the purge and trap and before any samples are run, the vial gripper must be calibrated. The "Auto Calibration" procedure (see Section 6.4) will establish the correct coordinate position setting for removal and replacement of sample vials in the sample tray, water vial sampling station, soil/solid sampling station, and the equilibrium ID station automatically. The calibrated vial gripper now ensures accurate vial movement.

Note: The "Auto Calibration" program does not calibrate the "Knockoff and Standard Clearance" heights. These coordinate settings must be checked manually. See "Vial 22 position", Section 5, or "Calibration Test", in Section 6.

2.14 Loop Calibration for Internal Standard

The absolute volume of the internal loop of the standard valve must be determined to achieve accurate sample data. The stated 1 µl volume is approximated within the stated tolerance from the valve manufacturer. For absolute internal standard accuracy, use the following calibration procedure before beginning your sample analysis.

1. Prepare a reference standard equivalent to a 1 µl volume injection via the valve.
2. Run the calibration standard by hand (put 5 ml directly into the sparge tube.
3. Run blanks in the Archon manual mode. Note: Be sure the manual mode program calls for internal standard when running the blanks.
4. Calibrate the internal standard data by comparing the Archon data to the hand standard.

2.15 Installation Checklist

Verify the following during and after installation of the Archon.

- ☐ Be certain the sample tray is pushed all the way to the rear most position in the cabinet.
- ☐ Confirm the supply helium pressure is between 60-90 PSI ± 5 PSI.
- ☐ Be certain the handle, on the black sample valve located on top of the sparge vessel, is rotated in the position of the water transfer line.
- ☐ Do not overtighten the cap on the blank/wash bottle. To properly tighten the cap, turn it until snug, then stop.
- ☐ Be certain the septum used for the soil samples is P/N DY-504104-00. It is extremely important that this low bleed septum is used because it is formulated for maximum sealing ability with minimum bleed of siloxane compounds that might interfere with chromatographic results.

Appendix No. 2 - Surrogate Loop Calibration for the Archon

Archon Rotor Size Determination

Required when calibrating surrogates within the curve - when rotor is not exactly 1 ul

Configuration:	*Initial*	
Std 1	IS @	250 ppm
Std 2	SS @	250 ppm
	Sample Vol	5 ml

Procedure

Step 1	Analyze calibration curve adding IS only from the Archon Calibrate surrogates within the curve
Step 2	Analyze 3 blanks or CC's adding IS and SS (Std 1 and Std 2)
Step 3	Quantitate the blanks or CC's based on the Calibration Curve
Step 4	Obtain an average recovery result and back calculate to volume added

Note: The determined rotor size is an approximate value (Based on average recoveries)

Rotor Size Calculation Table

	Trial 1	Trial 2	Trial 3	Average
SS1	0.00	0.00	0.00	0.00
SS2	0.00	0.00	0.00	0.00
SS3	0.00	0.00	0.00	0.00
			Overall Avg	0.00

(Smpl Vol) : (Avg Rec) = ([SS]) (x)

where x = rotor size

rotor size= 0.00 ul

Rotor Size Calculation Table - Example

	Trial 1	Trial 2	Trial 3	Average
SS1	53.25	52.15	53.76	53.05
SS2	54.12	55.32	54.85	54.76
SS3	53.65	52.45	54.75	53.62
			Overall Avg	53.81

(Smpl Vol) : (Avg Rec) = ([SS]) (x)

where x = rotor size

rotor size= 1.08 ul

Professional Technical Services

Appendix 3 - Recommended VOC Sample Preservation Techniques and Holding Times

Sample Matrix	Preservative	Holding Time	Comment
Aqueous Samples With No Residual Chlorine Present	Cool to 4 ± 2°C.	7 days	If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples With No Residual Chlorine Present	Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
Aqueous Samples With Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to 4 ± 2°C.	7 days	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples With Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$	14 days[1]	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. Caution: never add acid preservative directly to a dechlorinating agent prior to sample collection.
Solid Samples[2]	Sample is extruded into an empty sealed vial and frozen on-site to < -7°C.	14 days[1]	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Appendix 3 - Recommended VOC Sample Preservation Techniques and Holding Times Cont.

Sample Matrix	Preservative	Holding Time[1]	Comment
Solid Samples[2]	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C for no more than 48 hours then frozen to < -7°C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C for no more than 48 hours then preserved with methanol upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not preserved with methanol prior to the expiration of the 48 hour period.
	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C.	48 hours	
	Cool to 4 ± 2°C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Freeze to < -7°C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and frozen on-site to < -7°C.	14 days[1]	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and cooled to 4 ± 2°C for 48 hours or less then frozen to < -7°C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Appendix 3 - Recommended VOC Sample Preservation Techniques and Holding Times Cont.

Sample Matrix	Preservative	Holding Time[1]	Comment
Solid Samples[2]	Sample is extruded into a vial containing reagent water and 1 g $NaHSO_4$ and cooled to 4 ± 2°C.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
	Sample is extruded into a vial containing methanol and cooled to 4 ± 2°C.	14 days[1]	Additional methanol extract storage time beyond 14 days may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

[1] A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

[2] For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours of sample collection.

STANDARD OPERATING PROCEDURE

Analysis of Semivolatiles by GCMS

Methods: EPA 8270C & 8270D

SOP NUMBER:	PGH-O-001-9
REVIEW:	Tim Harrison
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-O-001-8
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager — 08/19/15 Date

Senior Quality Manager — 08/19/15 Date

Department Manager/Supervisor — 08/19/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

1. Purpose

1.1 This SOP describes the procedure to be used for the GC/MS analysis of organic extracts for semivolatile parameters by EPA Method 8270C and 8270D.

2. Scope and Application

2.1 This procedure can be used to quantitate most acidic and base/neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivitization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. A complete list of compounds and their characteristic ions that may be analyzed according to this method can be found in Table 1. In most cases, this method is not appropriate for the quantitation of multicomponent analytes (e.g., Aroclors, Toxaphene, Chlordane, etc.), because of limited sensitivity for those analytes. When these analytes have been identified by another technique, this method is appropriate for confirmation for the presence of these analytes when concentration in the extract permits.

2.2 This procedure is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, and water samples. The following matrices and the associated methods are accepted for the preparation of samples to be analyzed by gas chromatography/mass spectrometry (GC/MS):

Matrix	Methods
Water	"Organic Extraction of Aqueous Samples by Separatory Funnel", EPA Method 3510C
Soil	"Microwave Extraction of Solids", EPA Method 3546
Waste	"Waste Dilution", EPA Method 3580A
TCLP	"Solid Phase Extraction (SPE) of Semivoa from TCLP Extracts", EPA Method 3535 and 3535A

2.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent extraction and exhibits poor chromatographic behavior. Under the alkaline conditions of the extraction step, a-BHC, g-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and can not be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

2.4 A list of the typical compounds (Target Analytes) and their reporting limits can be found in Table 7. Current MDLs are listed in LIMS and are available from the Quality Department.

3. Summary of Method

3.1 Samples are prepared for analysis by GC/MS using the appropriate sample preparation and, if necessary, sample cleanup procedures. Aqueous sample are prepared as per SOP PGH-O-028, Separatory funnel extraction. Solid samples are extracted as per SOP PGH-O-022, Microwave extraction. The sample is introduced into the GC/MS by injecting the extract into a gas chromatograph (GC) equipped with a narrow-bore fused-silica capillary column. The GC column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph. Analytes eluted from the capillary column are introduced into the mass spectrometer through a direct connection (heated interface). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (minimum) calibration curve.

4. Interferences

4.1 Sources of interferences in this procedure can be grouped into two broad categories: contaminated solvents, reagents and sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces.

4.1.1 Interferences co-extracted from the samples will vary considerably from sample to sample. While general cleanup techniques are referenced as part of this SOP, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

4.1.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

4.2 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples (e.g., GPC cleanup) and take corrective action to eliminate the problem.

4.3 Contamination by carryover can occur whenever high concentration and low concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between the sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a methylene chloride blank to check for cross-contamination. It may also be helpful to stop the sample run sequence and increase the oven temperature to 300 - 325°C for 15-30 minutes before proceeding with the next sample analysis.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc Quality Manual for the definitions used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Sample Storage: Information regarding EPA recommended holding times and storage conditions may be found in the appropriate PASI SOP for extraction. Unless specified by the client or by method requirements, samples are typically not stored beyond 30 days of the final project report date.

8.2 Extract Storage: Semivolatile sample extracts shall be stored at less than -10°C for method 8270C and 6°C or less for method 8270D, protected from light, in sealed vials

(e.g., crimp-capped vials) equipped with unpierced PTFE-lined septa. At no time shall sample extracts be stored along with stock standard solutions, pure standard materials, or matrix and surrogate spiking materials of any kind.

8.2.1 Semivolatile sample extracts are maintained in the laboratory for a period of not less than 30 days from the day the final report is sent to the client.

8.2.2 Sample extracts must be analyzed within 40 days of the extraction date.

9. Equipment and Supplies

9.1 Gas chromatograph/mass spectrometer system

9.1.1 Gas chromatograph: A Hewlett-Packard (HP) 5890 or 6890, or equivalent, temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source via a heated interface.

9.1.2 Column: 20m x 0.18mm ID 0.18µm film thickness silicone-coated fused-silica capillary column (Restek RTX-5Sil MS. (or equivalent).

9.1.3 Mass spectrometer: An HP 5973 or equivalent mass selective detector (MSD) capable of meeting method requirements. This system must be capable of meeting tuning criteria for decafluorotriphenylphosphine (DFTPP) as set forth in Table 3 of this procedure when 1µL the GC/MS tuning standard is injected through the GC (5-50ng of DFTPP).

9.1.4 GC/MS Interface: A heated, capillary-direct interface that achieves acceptable tuning performance criteria.

9.1.5 Data system: A HP Chemstation® computer system or equivalent is interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer is equipped with Target® or equivalent software that can search any GC/MS data file for ions of a specific mass and is capable of plotting such ion abundances versus time or scan number (EICP plot). The software allows integration of the abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also available on one or more operating systems in the Semivolatile laboratory

9.2 Syringes: 1.0mL, 250µL, 25µL and 10µL.

9.3 Volumetric flasks, - Appropriate sizes with ground-glass stoppers, Class A, glass.

9.4 Balance - Analytical, capable of weighing 0.0001g.

9.5 Vials - 10mL amber glass with PTFE-lined screw caps.

9.6 Amber and clear 1mL crimp-top sample vials with PTFE-lined crimp tops.

9.7 Vial crimper and decapper.

9.8 5 ¾ inch disposable pipettes.

9.9 Kimwipes®,or equivalent.

10. Reagents and Standards

10.1 Reagent grade inorganic chemicals and (Fisher Optima® grade, equivalent or higher grade) organic solvents shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on

Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.2 Standards

10.2.1 Certificates of Analysis (COAs): When standards are received from outside vendors they are accompanied by a Certificate of Analysis (COA). Each COA is assigned a unique reference number which is entered into the standards log book. The COAs are then placed in a binder maintained in the laboratory.

10.2.2 Refer to the Semivolatile Standard Logbook for the specific procedure for preparing each of the solutions listed below.

10.2.3 Most stock standard solutions are purchased from Restek (or an equivalent vendor) as certified, commercially prepared solutions. Upon initial use, whatever remains of the commercially-prepared stock solutions are transferred to 1mL, amber, screw-top or crimp-top vials labeled with the unique identification number, the final concentration of the solution, the date the solution was prepared and the initials of the analyst responsible for preparing the solution. Store them away from light in the manufacturer's recommended conditions.

10.2.3.1 Stock standard solutions shall be checked upon each use for signs of degradation or evaporation. Some typical indicators of degradation include color change and precipitate present in the vial. Stock standard solutions must be replaced upon the manufacturer's expiration date, after 1 year from the opened date (unless the manufacturer's date is earlier) or whenever comparison with Quality Control check samples indicates a problem.

10.2.3.2 All stock standard solutions and calibration mixes prepared by the analyst shall be documented in a standard logbook, which may be found in the Semivolatile laboratory. Entries must include a unique identification number for each vial of standard material prepared along with the purity or concentration of the stock used, the expiration date of the stock used, the lot number of both the material used, all solvents used to prepare the solution, the amount of stock or material used, the final volume of the solution generated, the final concentration of the solution, the date the solution was prepared and the initials of the analyst responsible for preparing the solution(s).

10.2.3.3 Occasionally, the Semivolatile Department will prepare solutions to be used for MDL determinations and spiking solutions. The above information for the stock materials may be recorded in the Semivolatile standard log book. All of the above information for the working solutions shall be recorded in the log book and the actual spiking and MDL solutions shall be stored in the Organic Preparation laboratory.

10.2.4 Internal standard solutions

10.2.4.1 The internal standards used are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d10, chrysene-d_{12}, and perylene-d_{12} (see Table 5).

10.2.4.2 Commercially prepared solutions of internal standards at a concentration of 2000mg/L are purchased and diluted to a concentration of 200mg/L at the laboratory. These are in a methylene chloride solution.

10.2.4.3 Internal standards are spiked into standard solutions and samples at a concentration of 4mg/L, (e.g., 500µL sample is placed in a separate 1mL vial and spiked with 10µL of the 200mg/L internal standard solution).

10.2.4.4 Internal standard solutions are stored in conical vials equipped with Mininert valves at < -10°C when not in use.

10.2.5 GC/MS tuning standard

10.2.5.1 The tuning standard is a methylene chloride solution containing 5.0mg/L of DFTPP. It also contains 4,4'-DDT, pentachlorophenol, and benzidine and is provided from a commercially prepared solution (1000mg/L) in order to verify injection port inertness and GC column performance. Store at -10^{o}C or less when not in use.

10.2.6 Working calibration standards

10.2.6.1 Typically seven calibration standards are prepared at different concentrations. The concentration range used for most Target Compound List (TCL) analytes is 1-20mg/L. An example of the standard concentrations used in this range is 1mg/L, 2mg/L, 4mg/L, 8mg/L, 12mg/L, 16mg/L and 20mg/L. Dilutions of stock standards are prepared by using an adequately sized syringe. Recommendations are a syringe capable of measuring at least twice the volume needed, but not more than 10 times the volume. The calculated amount of stock solution is added to the appropriate solvent in order to achieve the desired working range concentrations and volumes. (See the SVOA Standard logbooks for the amounts and volumes currently in use)

10.2.6.2 For working range concentrations, generally 500µL solutions are prepared in amber crimp top vials. For most compounds, the 1mg/L calibration standard multiplied by the solution factor of the sample corresponds to the sample concentration at or below that necessary to meet the data quality objectives of the project (i.e., 1mg/L x 330 = 330µg/Kg detection level (DL) for phenol in soil). This level may be higher (e.g., 800µg/Kg DL for 2-nitroaniline in soil). The remaining standards correspond to the range of concentrations found in actual samples and do not exceed the working range of the GC/MS system. Other initial calibration standards containing various analytes at varying concentrations may be used to satisfy both the method requirements and the client's needs.

10.2.6.3 An initial calibration standard curve is prepared and analyzed for each analyte of interest. This may include analyzing more than one set of initial calibration curves, each containing different target analytes. These target analytes may not include the entire list of analytes for which the method has been demonstrated, but at a minimum, shall contain all target analytes for which results are to be reported. The laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

10.2.6.4 Each 500µL aliquot of the working calibration standard is spiked with 10µL of 200mg/L internal standard solution when they are prepared. All standards, except the calibration verification standard, are stored at -10^{o}C or colder. The calibration verification standard is stored at 4±2°C and should be prepared weekly for method 8270C and as necessary for 8270D. Working standards may be used for no longer than 6 months from their date of creation.

10.2.6.5 The mid-point concentrations of the initial calibration standards are used to verify system performance on a daily basis. The actual concentration used is strictly dependent on the concentration levels of the calibration curve analyzed. The analyst shall select a concentration that best represents the mid-point of the calibration curve(s) analyzed. Midpoint concentrations should be prepared weekly.

10.2.7 Surrogate standards (Deuterated Monitoring Compounds (DMCs))

10.2.7.1 The surrogates used for this method are phenol-$d_{6,}$ 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. These are included in the working standards and are present in all sample extracts (see the appropriate extraction procedure for surrogate storage conditions). The final concentration of the acid surrogates in the aqueous sample extracts is 7.5ppb while the concentration of the B/N surrogates is 5ppb. The final concentration of the acid surrogates in the solid sample extracts is 2500ppb while the concentration of the B/N surrogates is 1667ppb.

10.2.8 Spiking standards

10.2.8.1 For most samples analyzed, the CLP Matrix Spiking Solution plus the PAHs is used and is applicable to this method. Refer to Table 2 for a list of these compounds and refer to Table 6 for acceptance criteria for percent recoveries. Client-specific requirements may dictate that all target analytes, Table 7, be in the matrix spiking solution. The final concentration of the analytes spiked in the aqueous extracts is 5-10ppb while the concentration in the solid extracts is 3330ppb.

11. Calibration

11.1 Establish operating conditions for analytes of interest based on recommendations by instrument manufacturers and column vendors, as well as Method 8270C and 8270D. An example of conditions for TCL analytes are:

11.1.1 Mass range: 35-500 amu.

11.1.2 Scan time: 1 sec/scan.

11.1.3 Initial temperature: 40 or 50°C (depending on instrument) hold for 1 minute.

11.1.4 Temperature program: ramp to 330°C at 15°C/min.

11.1.5 Final temperature: 345°C, hold until benzo[g,h,i]perylene elutes.

11.1.6 Injector temperature: 250-280°C.

11.1.7 Transfer line temperature: 280°C.

11.1.8 Source temperature: According to manufacturer's specifications.

11.1.9 Injector: Splitless mode.

11.1.10 Injection volume: 1-2µL (depending on instrument method).

11.1.11 Carrier gas: Helium.

11.1.12 Slight variations of the operating conditions are necessary in order to optimize performance for each MSD model in use.

11.2 **Tuning – Methods 8270C and 8270D**

11.2.1 Prior to analysis of the initial calibration standards, the GC/MS system is hardware-tuned using a 5.0mg/L injection of tuning mixture containing DFTPP, 4,4'-DDT, pentachlorophenol and benzidine. Analysis of initial calibration standards and samples shall not begin until the tuning criteria are met.

11.2.2 The mass spectrum needed to evaluate the success of DFTPP tuning is acquired as follows: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction is designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

11.2.3 The DFTPP tune acceptance criteria are listed in Table 3 for method 8270C and in Table 3A for method 8270D. The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20% for 8270D and 15% for 8270C..

11.2.4 The GC/MS tuning standard solution is also used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and peak tailing criteria for each will be used to evaluate if maintenance is needed (Suggested tailing factors of <3 and <5, respectively, for method 8270C and <2 for method 8270D). Use the manufacturer's software routine for calculating peak tailing.

11.2.4.1 If degradation is excessive and/or poor chromatography is noted, the injection port liner may require cleaning or replacement. Liners are purchased from Restek or equivalent vendor. It may also be necessary to remove the first 2-3in of the capillary column.

11.2.4.2 Repeat the tuning procedure after injection port maintenance until all criteria are met for DFTPP. Additional reduction in length of the column may be necessary to achieve acceptable results. If the tuning criteria still are not met, refer to the instrument manufacturer's manual for possible solutions regarding optimizing hardware tuning. Tuning and calibrating the GC/MS system less than 12-24 hours (depending on the instrument model) after major maintenance procedures (column change or source cleaning) is not recommended or generally successful. All maintenance is to be recorded in the instrument maintenance logbook.

11.2.4.3 Documentation of the return to service after performing maintenance and a successful tune/calibration is to be documented in the instruments maintenance log.

11.2.5 Once a successful tune has been performed, calibration and/or sample injections must be made within 12 hours of the injection of the successful tune. Once this 12-hour period has expired, a new, successful tune must be performed before continuing with analysis.

11.2.5.1 NOTE: All subsequent standards, samples, and QC associated with a DFTPP tune must employ identical gas chromatograph and mass selective detector conditions that were used to acquire the tune.

11.2.5.2 All samples must be analyzed within the 12 hour time limit of the DFTPP. Any sample acquired outside of the limit must be reanalyzed.

11.3 **8270C - Initial Calibration (ICAL)**

11.3.1 Before the initial calibration is started, a successful tune must be performed. A successful ICAL must then be performed before sample analysis may be started.

11.3.2 Analyze 0.5 or 2µL aliquot (depending on the instrument) of each working calibration standard (containing internal standards). Tabulate the response for target analytes using the area of the primary characteristic ion for the target analyte, as indicated in Table 1, and the concentration for that analyte in that particular standard. A set of at least five calibration standards is necessary. For 2nd order quadratic curve a minimum of 6 calibration standards is required. The injection volume must be the same for all standards and subsequent sample extracts. The midpoint calibration standard of the ICAL is used to establish the retention time windows for each analyte. For each calibration level, calculate response factors (RFs) for each target analyte relative to one of the internal standards using the Target® software. The Target® software uses the following equation when calculating RF:

$$RF = \frac{AS\_x\_CIS}{AIS\_x\_CS}$$

Where:

AS = Peak area of the analyte or surrogate
AIS = Peak area of the internal standard.
CS = Concentration of the analyte or surrogate, in ug/mL.
CIS = Concentration of the internal standard, in ug/mL.

11.3.3 The internal standards included in each standard and sample should permit most of the components of interest to have retention times of ±0.5 minutes (30 seconds) relative to one of these internal standards. Use the area associated with the base peak ion from the specific internal standard as the quantitation ion for the peak area in the above equation. See Table 5 for internal standards and their corresponding target analytes. If the analyte of interest to be quantitated, is not included in Table 5, use the internal standard that elutes closest to the analyte of interest.

11.3.4 Calculate the mean (average) response factor (mRF) and the percent relative standard deviation (RSD) for each target analyte and surrogate compound. If all analyte RSDs in the initial calibration are < 15% for 8270C, then all analytes may use average response factor for calibration. The Target® software uses the following equations when calculating mRF and RSD:

$$mRF = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where:

RF = response factor as calculated above
n = number of standard levels used for that analyte

$$RSD = \frac{SD}{mRF} x100$$

Where:

SD = the population standard deviation of the RF's
mRF = mean response factor as calculated above

11.3.5 Linearity of target analytes

11.3.5.1 The %RSD should be less than or equal to 15% for each target analyte for 8270C, except the Calibration Check Compounds (CCC) for 8270C only (see Table 4) which MUST be less than 30%. .

Note: For GC/MS calibration, Method 8270C requires 15% RSD as evidence of sufficient linearity to employ an average response factor. For the following compounds, some project QAPPs may allow a >15% RSD: Benzyl alcohol, 4-Chloroaniline, Hexachlorocyclopentadiene and 3,3-Dichlorobenzidine.

11.3.5.2 When target analytes are >15% for 8270C, (or >15% for the above compounds), linear or quadratic fits may be used. Performing a linear regression ($r \geq 0.99$ or better) or a weighted least squares regression ($r \geq 0.99$ or better) must be employed to achieve linearity. A weighted curve is often recommended; unweighted regressions are likely to have high relative errors at the lower concentration levels and are strongly discouraged. Weighted regressions should be used whenever possible.

11.3.5.3 For 2nd order curves such as quadratic, the coefficient of determination (COD or r^2) $r^2 \geq 0.99$. 2nd order curves should only be used in circumstances where a linear curve is clearly not appropriate. While quadratic curves are generally reliable within the calibration range, they can produce highly erroneous results above the calibration range including negative numbers at high concentrations. If a quadratic curve is used, each and every calibration plot must be visually inspected to ensure that the fitted function does not re-curve producing multiple concentrations for a single instrument signal.

11.3.5.4 Continuing calibration for those parameters that are evaluated by linear regression or other fits must be determined by the percent drift or percent difference calculation.

11.3.6 8270C Low Level Standard Read back for Linear Curve and quadratic fit :

The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. Analytes using linear calibration fit and quadratic fit should have the read back concentration of the low level standard evaluated. The read back concentration should be within 30% of the true value. Any sample with detects for analytes that fail the read back criteria, and are using linear or quadratic calibration must be flagged as estimated, or described in the narrative. Flagging is not required for any samples with non-detects for analytes that fail the read back criteria.

11.3.7 For 8270C: System Performance Check Compounds (SPCCs)

11.3.7.1 The minimum mRFs must be met in the ICAL before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are:

- N-nitroso-di-n-propylamine;
- hexachlorocyclopentadiene;
- 2,4-dinitrophenol;
- 4-nitrophenol.

11.3.7.2 The minimum acceptable mRF for these compounds is 0.050. These SPCCs typically have very low mRFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

11.3.7.3 If the minimum mean response factors are not met, the system must be reevaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites in the column or chromatographic system, and/or contaminated source. Usually injection port maintenance is a successful solution to this problem and should be attempted first, prior to preparing new standard solutions. The requirements for this check must be met before sample analysis begins.

11.3.8 For 8270C: Calibration Check Compounds (CCCs).

11.3.8.1 The ICAL must be examined to determine if the CCCs listed in Table 4 meet the minimum requirements.

11.3.8.2 The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes.

11.3.8.3 The RSD for each individual CCC must be less than or equal to 30%. If the RSD of any CCC is greater than 30% then the chromatographic system is too reactive for analysis to begin. Perform maintenance and repeat the calibration procedure from the beginning. Possible problems are the same as listed for SPCCs above.

11.3.8.4 If the CCCs are not included in the list of analytes for a project then each analyte of interest must have an RSD no greater than 30% in order for analysis to begin.

11.3.8.5 NOTE: the analytes of interest must still meet the “linearity of target analytes” criteria below for reporting purposes.

11.3.9 Evaluation of retention times

11.3.9.1 The retention time of the internal standards shall not vary by more than 30 seconds from the midpoint standard of the ICAL.

11.3.10 If the RSD of any target analyte (including the CCCs) is greater than 15% for method 8270C and positives for the analyte have been identified in the sample, the sample must be reanalyzed on a system which meets the %RSD criteria for the target analyte of interest. Also the curve may be evaluated using the other types of curves such as linear regression. Alternatively, a new initial calibration must be performed. This may require preparing and analyzing a separate calibration curve over a narrower linear range for an analyte.

11.3.10.1 There may be times when it proves necessary to report positive results for an analyte from a non-linear ICAL. In this circumstance, the result must be flagged on the report as an estimated concentration. Further method development may be

required to improve performance for compounds that routinely exhibit such characteristics.

11.3.11 A sample result may be reported as non-detect without qualification provided there is adequate sensitivity to detect the compound is present in the ICAL at the reporting limit.

11.3.12 When the RSD exceeds 15% for 8270C, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit chromatographic behavior, etc.

11.3.13 Second source standard verification (ICV)

11.3.13.1 Immediately after the initial calibration curve has been analyzed, the standards used for the ICAL must be verified by the injection of a second source standard (ICV). This standard will be a mid-point calibration concentration (8mg/L) prepared from stock solutions obtained from a vendor independent of the initial calibration stock solution vendor. Review the 2nd source results for significant signs of degradation or standard preparation errors before the analysis of any samples. File the results of this verification with the results of the ICAL.

11.3.13.2 For 8270C: The ICV limits are 80-120%. Target analytes failing the 20% criteria must be flagged as estimated values.

11.3.14 When all of the ICAL and calibration verification criteria have been met, sample analysis may be performed within the remainder of the 12-hour tune period.

11.3.15 The following compounds may require special treatment when being determined by this procedure:

11.3.15.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

11.3.15.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

11.3.15.3 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

11.3.15.4 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

11.3.15.5 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with a high boiling material.

11.3.15.6 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature, as the performance of other analytes may be adversely affected.

11.3.15.7 In addition, analytes in the list provided above are flagged on initial calibration and daily calibration checks when there are limitations caused by chromatographic problems.

11.4 **8270D - Initial Calibration (ICAL)**

11.4.1 Before the initial calibration is started, a successful tune must be performed. A successful ICAL must then be performed before sample analysis may be started.

11.4.2 Analyze 0.5 or 2µL aliquot (depending on the instrument) of each working calibration standard (containing internal standards). Tabulate the response for target analytes using the area of the primary characteristic ion for the target analyte, as indicated in Table 1, and the concentration for that analyte in that particular standard. A set of at least five calibration standards is necessary. For 2nd order quadratic curve a minimum of 6 calibration standards is required. The injection volume must be the same for all standards and subsequent sample extracts. The midpoint calibration standard of the ICAL is used to establish the retention time windows for each analyte. For each calibration level, calculate response factors (RFs) for each target analyte relative to one of the internal standards using the Target® software. The Target® software uses the following equation when calculating RF:

$$RF = \frac{AS\_x\_CIS}{AIS\_x\_CS}$$

Where:

AS = Peak area of the analyte or surrogate
AIS = Peak area of the internal standard.
CS = Concentration of the analyte or surrogate, in ug/mL.
CIS = Concentration of the internal standard, in ug/mL.

11.4.3 The internal standards included in each standard and sample should permit most of the components of interest to have retention times of ±0.5 minutes (30 seconds) relative to one of these internal standards. Use the area associated with the base peak ion from the specific internal standard as the quantitation ion for the peak area in the above equation. See Table 5 for internal standards and their corresponding target analytes. If the analyte of interest to be quantitated, is not included in Table 5, use the internal standard that elutes closest to the analyte of interest.

11.4.4 Calculate the mean (average) response factor (mRF) and the percent relative standard deviation (RSD) for each target analyte and surrogate compound. If all analyte (Table 7) RSDs in the initial calibration are < 20% for 8270D, then all analytes may use average response factor for calibration. The Target® software uses the following equations when calculating mRF and RSD:

$$mRF = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where:

RF = response factor as calculated above
n = number of standard levels used for that analyte

$$RSD = \frac{SD}{mRF} x100$$

Where:

SD = the population standard deviation of the RF's
mRF = mean response factor as calculated above

11.4.5 Linearity of target analytes

11.4.5.1 The %RSD for 8270D should be less than or equal to 20% for each target analyte, Table 7.

11.4.5.2 When target analytes RSD are >20% for 8270D, linear or quadratic fits may be used. Performing a linear regression ($r \geq 0.99$ or better) or a weighted least squares regression ($r \geq 0.99$ or better) must be employed to achieve linearity. A weighted curve is often recommended; unweighted regressions are likely to have high relative errors at the lower concentration levels and are strongly discouraged. Weighted regressions should be used whenever possible.

11.4.5.3 For 2nd order curves such as quadratic, the coefficient of determination (COD or r^2) $r^2 \geq 0.99$. 2nd order curves should only be used in circumstances where a linear curve is clearly not appropriate. While quadratic curves are generally reliable within the calibration range, they can produce highly erroneous results above the calibration range including negative numbers at high concentrations. If a quadratic curve is used, each and every calibration plot must be visually inspected to ensure that the fitted function does not re-curve producing multiple concentrations for a single instrument signal.

11.4.5.4 Continuing calibration for those parameters that are evaluated by linear regression or other fits must be determined by the percent drift or percent difference calculation.

11.4.6 8270D Minimum Response Factors: It is also required that a minimum response factor for the most common target analytes, as noted in Table 8, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity.

11.4.6.1 Any individual analyte that fails the minimum response factor (see Table 8) must have a demonstration of sensitivity in the analytical batch to report non-detects. Detected results may be reported without qualification. The demonstration of sensitivity is analysis of a low level CCV (LLCCV) at or below the reporting limit. The criterion for passing a LLCCV is detection only and a passing LLCCV allows non-detects to be reported without flagging. The LLCCV would be analyzed immediately after the mid-level CCV. In general, Table 8 is used for the minimum response factors criteria.

11.4.7 8270D Low Level Standard Read back for Linear Curve and quadratic fit :

The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. Analytes using linear calibration fit and quadratic fit should have the read back concentration of the low level standard evaluated. The read back concentration should be within 30% of the true value. Any sample with detects for analytes that fail the read back criteria, and are using linear or quadratic calibration must be flagged as

estimated, or described in the narrative. Flagging is not required for any samples with non-detects for analytes that fail the read back criteria.

11.4.8 Evaluation of retention times

11.4.8.1 The retention time of the internal standards shall not vary by more than 30 seconds from the midpoint standard of the ICAL.

11.4.9 For 8270D: It is understood that due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet the 20% RSD or 0.99 correlation coefficient criteria. It is acknowledged that the failing compounds may not be critical to a specific project and therefore may be used as qualified data or estimated values.

11.4.9.1 If more than 10% of the compounds in the initial calibration exceed the 20% RSD and do not meet the minimum correlation coefficient (0.99), analysis cannot begin as the chromatographic system is considered too reactive. Perform maintenance and repeat the calibration procedure from the beginning.

11.4.10 If the RSD of any target analyte is greater than 20% for method 8270D and positives for the analyte have been identified in the sample, the sample must be reanalyzed on a system which meets the %RSD criteria for the target analyte of interest. Also the curve may be evaluated using the other types of curves such as linear regression. Alternatively, a new initial calibration must be performed. This may require preparing and analyzing a separate calibration curve over a narrower linear range for an analyte.

11.4.10.1 There may be times when it proves necessary to report positive results for an analyte from a non-linear ICAL. In this circumstance, the result must be flagged on the report as an estimated concentration. Further method development may be required to improve performance for compounds that routinely exhibit such characteristics.

11.4.11 A sample result may be reported as non-detect without qualification provided there is adequate sensitivity to detect the compound is present in the ICAL at the reporting limit.

11.4.12 When the RSD exceeds 20% for 8270D, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit chromatographic behavior, etc.

11.4.13 Second source standard verification (ICV)

11.4.13.1 Immediately after the initial calibration curve has been analyzed, the standards used for the ICAL must be verified by the injection of a second source standard (ICV). This standard will be a mid-point calibration concentration (8mg/L) prepared from stock solutions obtained from a vendor independent of the initial calibration stock solution vendor. Review the 2nd source results for significant signs of degradation or standard preparation errors before the analysis of any samples. File the results of this verification with the results of the ICAL.

11.4.13.2 For 8270D: The ICV limits are 70-130%. Target analytes failing the 30% criteria must be flagged as estimated values.

11.4.14 When all of the ICAL and calibration verification criteria have been met, sample analysis may be performed within the remainder of the 12-hour tune period.

11.4.15 The following compounds may require special treatment when being determined by this procedure:

11.4.15.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

11.4.15.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

11.4.15.3 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

11.4.15.4 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

11.4.15.5 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with a high boiling material.

11.4.15.6 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature, as the performance of other analytes may be adversely affected.

11.5 In addition, analytes in the list provided above are flagged on initial calibration and daily calibration checks when there are limitations caused by chromatographic problems.

11.6 Table 11 summarized the calibration and QA/QC Requirements for method 8270D.

11.7 **Removal of Points from a Calibration Curve:**

11.7.1 Removing or replacing levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. The curve is evaluated with the levels removed. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve must be reanalyzed. Corrective action may include instrument maintenance and/or repreparation of standards. If the low standard is dropped, then the lowest remaining calibration point must be at or below the reporting limit.

11.8 **Basic Elements of Calibration Review:**

11.8.1 The lowest calibration level must be at or below the RL. If this requirement is not met the instrument must be recalibrated to include a lower concentration standard. The lowest calibration level must be higher than the MDL.

11.8.2 The minimum number of calibration points requirement must be met. A minimum of five calibration standards is required. For 2nd order quadratic curve a minimum of 6 calibration standards is required. If not the instrument must be recalibrated.

11.8.3 Linearity requirements as stated in this SOP must be met. If this requirement is not met, the problem must be investigated and the instrument recalibrated.

11.8.4 Examine the plots for quadratic fits: The calibration plots must be visually examined to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal.

11.8.5 Y-intercept: should be < 0.5 RL when reporting to the RL and < MDL when reporting to the MDL.

11.8.6 Increasing Response with Increasing Concentration: The instrument signal should increase with every increase in standard concentration.

11.9 **8270C - GC/MS calibration verification (CCAL or CCV)**

11.9.1 Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

11.9.2 Prior to the analysis of samples or calibration standards, a successful, tune must be performed. This tune MUST meet all criteria before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

11.9.3 The initial calibration for each compound of interest must be verified once every 12 hours prior to sample analysis, using the same analytical conditions used for the ICAL. This is accomplished by analyzing a calibration standard at a concentration at or near the midpoint concentration (8mg/L) of the calibrating range of the GC/MS. The results from this calibration standard must meet the following verification acceptance criteria.

11.9.3.1 NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.9.4 For 8270C: The percent difference (%D), or percent drift (%Drift), for all CCCs must be less than or equal to 20%. All other target analytes, it must be less than or equal to 40%.

11.9.5 For 8270C: SPCC's - Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

11.9.5.1 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

11.9.5.2 The most common cause of this problem is active sites in the injection port. Attempt injection port maintenance first. This may include insert replacement, gold seal replacement and removing 2-3" of the front of the column. If this still fails to correct the problem, as much as 1 meter of column may need to be removed from the front of the column. Failure to correct the problem after removing significant amounts of the front of the column usually indicates that the column needs to be replaced.

11.9.6 For 8270C: Calibration check compounds (CCCs)

11.9.6.1 After the SPCC criteria are met, the CCCs listed in Table 4 are used to check the validity of the initial calibration. This is accomplished by evaluation of the calibration check standard on the Target® or equivalent software using percent difference (%D). The %D or the %Drift is calculated between the RF from the CCAL and the mRF from the ICAL.

11.9.6.2 If the percent difference, or percent drift, for each CCC is less than or equal to 20% then sample analysis may continue. If any one CCC has a %D, or %Drift that is greater than 20% then corrective action

must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, and are not included in the calibration standards, then all of the analytes of interest must meet the 20% criteria.

11.9.6.3 Problems similar to those listed under SPCCs could affect the CCCs and the analytes of interest. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

11.9.6.4 The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds (0.5 minutes) from that in the mid-point standard of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.9.6.5 If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (e.g., -50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.9.6.6 A method blank will be analyzed after calibration standards and prior to field sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants interferences from the analytical system including glassware and reagents. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. The need for this may be determined by the individual analyst familiar with the current analytical conditions of the system and in accordance with the system's expected level of performance. See Section 15 of this SOP for method blank performance criteria.

11.9.6.7 NOTE: A major source of GC/MS system contamination occurs, though infrequently, in the autosampler injector. Attempt to remove the contamination by replacing the sample syringe. If the problem persists, change the solvent rinse, waste vials and diffusion caps.

11.10 **8270D - GC/MS calibration verification (CCAL or CCV)**

11.10.1 Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

11.10.2 Prior to the analysis of samples or calibration standards, a successful, tune must be performed. This tune MUST meet all criteria before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

11.10.3 The initial calibration for each compound of interest must be verified once every 12 hours prior to sample analysis, using the same analytical conditions used for the ICAL. This is accomplished by analyzing a calibration standard at a concentration at or near the midpoint concentration (8mg/L) of the calibrating

range of the GC/MS. The results from this calibration standard must meet the following verification acceptance criteria.

11.10.3.1 NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.10.4 For 8270D: The percent difference, or percent drift, for all target analytes, Table 7, must be less than or equal to 20%.

11.10.4.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 8. This criterion is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration. All other target compounds not listed in Table 8 must have a minimum RRF of ≥ 0.01.

11.10.4.2 If the percent difference or drift is greater than 20% for more than 20% of the compounds included in the initial calibration, corrective action must be taken prior to sample analysis. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

11.10.4.3 If the percent difference or percent drift of any target analyte is greater than 20% and positives for the analyte have been identified in the sample, the sample must be reanalyzed on a system which meets the % difference or drift criteria for the target analyte of interest or the result must be flagged on the final report as an estimated concentration.

11.10.4.4 Any individual analyte that fails the minimum response factor (see Table 8) must have a demonstration of sensitivity in the analytical batch to report non-detects. The demonstration of sensitivity is analysis of a low level CCV (LLCCV) at or below the reporting limit (See also section 11.4.7). The LLCCV would be analyzed immediately after the mid-level CCV. The criterion for passing a LLCCV is detection only and a passing LLCCV allows non-detects to be reported without flagging. If the compounds failing the 20% criterion are positive, then the results are qualified as estimated using a qualifier. Any compound with a %D or %Drift >20% must be narrated.

11.10.4.5 The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds (0.5 minutes) from that in the mid-point standard of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.4.6 If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (e.g., -50% to + 100%) from that in the mid-point standard level of the most recent

initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.4.7 A method blank will be analyzed after calibration standards and prior to field sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants interferences from the analytical system including glassware and reagents. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. The need for this may be determined by the individual analyst familiar with the current analytical conditions of the system and in accordance with the system's expected level of performance. See Section 15 of this SOP for method blank performance criteria.

11.11 NOTE: A major source of GC/MS system contamination occurs, though infrequently, in the autosampler injector. Attempt to remove the contamination by replacing the sample syringe. If the problem persists, change the solvent rinse, waste vials and diffusion caps.

11.12 Table 11 summarized the calibration and QA/QC Requirements for method 8270D.

12. Procedure

12.1 Organic sample preparation will provide sample extracts according to the appropriate extraction procedure and clean-up procedure. For sample preparation information, please refer to SOPs PGH-O-028 (sep funnel extraction), PGH-O-022 (microwave extraction), PGH-O-007 (solid phase extraction) and PGH-O-011 (waste dilution extraction)

12.2 GC/MS analysis of samples

12.2.1 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10uL of the 200mg/L internal standard solution to 0.5mL of concentrated sample extract obtained from sample preparation (the final concentration of the internal standard should be 4mg/L).

12.2.2 When the final sequence has been entered into the computer a copy of this page is printed.

12.2.2.1 Data files for samples are named according to instrument id number, date and file letter (e.g., M1081101). Tune injections are named similarly, but include the letter "T" and are numbered according to the number of tune injections made (e.g., M10811T1, M30811T2 and M30811T3, etc.) Standard injections will begin with the letter 'S' or 'Z' and are numbered sequentially.

12.2.3 Initiate an autosampler sequence in order to inject a 0.5 or 2µL (depending on the instrument and what was used for the ICAL) aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration. The volume to be injected should contain 5ng of base/neutral and 7.5ng of acid surrogates (assuming 100% recovery). The injection volume must be the same volume used for the calibration standards.

12.2.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (4mg/L).

12.2.4.1 All sample and QC surrogate recoveries are 'diluted out' at 5x dilution

12.2.4.2 NOTE: It is a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check for drift, method performance, poor injection, and to anticipate the need for system inspection and/or maintenance.

12.2.5 Check all samples for adequate surrogate and internal standard recoveries after the twelve-hour sample run is completed. In addition, be sure that all samples contained in a particular run sequence have been analyzed within the 12-hour tune period. Reanalyze any that are outside the 12-hour tune period.

12.2.6 The retention time (RT) of each surrogate must be within +/-0.06 relative retention time (RRT) of the RRT of the associated internal standard (no greater than +/- 10 seconds).

12.2.7 Area counts of the internal standard peaks in all samples, blanks and spikes must be between 50-200% of the area of the internal standard areas in the daily CCAL.

12.2.8 Internal standard retention time: The retention times of the internal standards in the samples must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds (0.5 minutes) from that in the calibration verification standard, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

12.3 Qualitative Analysis

12.3.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum (usually obtained from the daily CCAL or from the ICAL). The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

12.3.1.1 See the PGH SOP [PGH-Q-030] for the procedure to follow when performing manual integrations

12.3.2 The RT of the sample component is within +/-0.06 RRT of the RRT of the associated internal standard component (no more than +/-10 seconds)

12.3.3 All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion the spectrum equals 100 percent) must be present in the sample spectrum.

12.3.4 The relative intensities of the characteristic ions agree within 20% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 30% and 70%).

12.3.5 Structural isomers that produce similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between the two isomer peaks is less than 25% of the sum of the two peak heights. If this criterion is not met, results will be flagged or structural isomers may be identified as isomeric pairs (e.g., m/p-cresol).

12.3.6 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra are important. Examination of extracted ion current profiles (EICP) of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co-elute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

12.3.7 If a compound cannot be verified by all of the above criteria, but in the technical judgment of the GC/MS operator (in conjunction with the supervisor) the identification is correct, the peak may be reported as a positive identification.

12.4 Quantitative analysis

12.4.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

12.4.2 RF determination is 15% or less in the ICAL for method 8270C and 20% or less in the ICAL for method 8270D and the CCAL was within 20%D of the ICAL, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Section 14) as follows:

$$Concentration = \frac{(A_x)(I_s)}{(A_{IS})(MRF)} * (SF/DF)$$

Where:

Ax = Area of the characteristic ion for the compound (Table 1)
Ais = Area of the characteristic ion for the internal standard (Table 1 & 5)
Is = Concentration of the internal standard (μg/mL) in sample aliquot.
MRF = Mean response factor
SF/DF = Solution factor/dilution factor

12.4.3 Surrogate (DMCs) Standard Check: Determination of surrogate recoveries is accomplished by including the surrogate compounds in at least one of the sets of initial calibration standard solutions used to quantitate a particular group of samples. The surrogates are included at concentration levels that represent a range of concentrations that will encompass the expected surrogate concentrations in the samples. An initial calibration is generated for them as for the other target analytes.

12.4.3.1 The surrogate solution used to spike the samples is verified by preparing a portion of the solution as a sample (this usually requires a dilution) and analyzing it by GC/MS. The results are compared to the expected true value of the solution prior to use of the in samples. The %Recovery for the surrogates (CMCs) must meet the criteria listed in Table 6.

12.4.4 Matrix Spike Check: This procedure is the same as that performed for the surrogate spike check. The actual solution used to spike the samples is verified by preparing a portion of the solution as a sample (this usually requires a dilution) and analyzing it by GC/MS. The results are compared to the expected true value of the analytes. The spike recoveries and the relative percent difference between MS and MSD's must meet limits as established by the laboratory. The %Recovery for the matrix spikes must meet the criteria listed in Table 9.

12.5 Library Searches

12.5.1 When requested by the client, an NIST library search on the sample may be performed using the Thruput Target® software or equivalent for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

12.5.1.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

12.5.1.2 The relative intensities of the major ions should agree within $\pm$20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

12.5.1.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.5.1.4 Review the spectrum for possible background contamination or presence of co-eluting compounds if ions are present in the sample spectrum, but not in the reference spectrum.

12.5.1.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.

12.5.2 When requested by the client, the concentration of any non-target analytes tentatively identified in the sample may be estimated. The same formula as normal target analytes should be used with the following modifications: The areas, A_{is} and A_x, should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The resulting concentration will be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

13. Calculations

13.1 A solution factor (SF) is calculated by dividing the final volume of the extract (in mL) by the initial weight/volume of the sample (in g/mL) and multiplying by 1000. This SF is then multiplied by any dilution factors that were employed to produce a SF/DF number. The SF/DF is then multiplied by the on-column concentration as calculated by the Target software to produce the reportable concentration in µg/Kg or µg/L (See equation in Section 12.4.2).

13.2 Surrogate, MS and MSD recovery

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

NOTE: The SampleConc is zero (0) for the LCS and Surrogate Calculations

13.3 Relative Percent Difference (RPD)

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

Where: R1 = Result Sample 1
R2 = Result Sample 2

13.4 % DDT degradation = ((area DDD / DDE) / ((area DDD / DDE) + area DDT)) * 100

13.5 % Difference

$$\%D = \frac{TrueValue - MeasuredValue}{TrueValue} * 100$$

Where:
TrueValue = Amount spiked (can also be the CF or RF of the ICAL Standards)
Measured Value = Amount measured (can also be the CF or RF of the CCV)

13.6 % Drift

$$\%Drift = \frac{CalculatedConcentration - TheoreticalConcentration}{TheoreticalConcentrtion} * 100$$

13.7 Relative Retention Time (RRT): the ratio of the retention time of a compound to that of a standard (such as an internal standard).

RRT= RTc/RTis

Where:

RTc = Retention time for the semivolatile target or surrogate compound in continuing calibration.
RTis= Retention time for the internal standard in calibration standard or in a sample.

14. Quality Control

14.1 Each batch of samples will have an associated Method Blank (MB), Laboratory Control Sample (LCS), and a Matrix Spike/Matrix Spike Duplicate (MS/MSD) if there is sufficient sample.

14.2 Quality Control procedures necessary to evaluate the GC system operation are as follows:

14.2.1 The GC/MS system must be tuned to meet the DFTPP criteria listed in Table 3.

14.2.2 There must be an initial calibration of the GC/MS system.

14.2.3 The GC/MS system must meet the calibration verification acceptance criteria for each 12 hour tune period.

14.3 The Semivolatile Laboratory has procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). This includes the analysis of QC samples including a method blank, matrix spike, matrix spike duplicate, and a laboratory control sample (LCS) in each preparation batch (20 samples), or in accordance with specific method requirements, and the addition of surrogates to each field sample and QC sample. For most samples analyzed, the CLP Matrix Spiking Solution plus the PAHs is used and is applicable to this method. Refer to Table 2 for a list of these compounds and refer to Table 6 for acceptance criteria for percent recoveries. Some projects require the spiking of the specific compounds of interest, since the spiking compounds listed in this method would not be representative of the compounds of interest required for the project. When this occurs, matrix, MDL and LCS spiking standards which are representative of the compounds of interest are prepared in methanol, either by the Semivolatile group or the Organic Preparation group, with each compound present at a concentration appropriate for the project.

14.4 Client-specific requirements may dictate that all target analytes be in the matrix spiking solution (this may require the preparation and analysis of multiple LCS and MS/MSDs).

14.4.1 A method blank must not contain results for target analytes that are greater than the reporting limit (1/2 the reporting limit for client-specific requirements).

14.4.1.1 An MB with results above the reporting limit must be investigated to identify the source of the contamination and appropriate corrective measures must be taken and documented.

14.5 Tables 5 and 6 list the appropriate compounds and concentrations used for internal standards and surrogates. Spiking compounds are listed in Table 2.

14.5.1 The following criteria shall be used for determining the minimum number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a two (2) year period:

14.5.2 For methods that include 1-10 targets, spike all components.

14.5.3 For methods that include eleven 11-20 targets, spike at least ten (10) or 80%, whichever is greater.

14.5.4 For methods with more than 20 targets, spike at least sixteen (16) components.

14.6 **Allowable Marginal Exeedances**:

14.6.1 The LCS is spiked with the list of compounds listed in Tables 9 and 10. If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control, therefore corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits are established to determine when corrective action is necessary. A ME is defined as being beyond the LCS control limit (three standard deviations), but within the ME limits. ME limits are between three (3) and four (4) standard deviations around the mean. The number of allowable marginal exceedances is based on the number of analytes in the LCS. **If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary.** This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than eleven analytes.

14.6.2 The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
>90	5
71-90	4

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
51-70	3
31-50	2
11-30	1
<11	0

14.6.3 For method 8270C and 8270D if more than 90 compounds are spiked in the LCS the number of marginal exceedances allowed is five. The LCS control limits and the control limits for marginal exceedances are listed in Tables 9 and 10. **If more than 5 analytes exceed the LCS control limits and any one of the five compounds exceed the marginal exceedance limits, the LCS fails**.

14.6.4 If an LCS is spiked with fewer than 90 compounds, the number of allowed marginal exceedances changes as listed in the table in Section 14.6.2.

14.6.5 If the same analyte exceeds the LCS control limit consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken. A lab track (corrective action database) ticket must be generated describing the failure, root cause and corrective action.

14.7 Corrective Actions for Out-Of-Control Data

14.7.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.7.2 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.7.2.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.7.3 Matrix Spike Recovery (MS) – If the Matrix Spike recoveries do not meet the acceptance criteria, the batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the spike recovery is not within the 25% RPD, a note is included in LIMS.

14.7.4 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.7.5 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.7.6 Table 11 summarized the QA/QC Requirements for method 8270D.

15. Method Performance

15.1 Method detection limit (MDLs) studies are completed, or verified, annually for each sample matrix extracted and analyzed on a GC/MS system.

15.2 Practical quantitation limits (PQLs) and MDLs are calculated and determined using the data collected from the analysis of the extracted MDL samples.

15.3 Performance evaluation (PE) samples are routinely analyzed.

15.4 Surrogate recovery data are evaluated through comparison of individual samples versus the surrogate control limits adopted by the laboratory. These control limits are listed in Table 6.

15.4.1 Surrogate recoveries are acceptable when the percent recoveries for individual surrogate compounds are within the adopted control limits.

15.5 Matrix spike, matrix spike duplicate and LCS recovery data are evaluated through the comparison of the calculated percent recoveries versus the control limits established by the laboratory.

15.5.1 Up to date control limits are calculated and maintained using the percent recoveries from the last twenty (at a minimum) data points from previously analyzed matrix spike and matrix spike duplicate samples. These limits are updated and stored in the acode on LIMS.

15.5.2 Matrix spike, matrix spike duplicate and LCS recoveries are acceptable when the percent recoveries for individual spike/LCS compounds are within the established control limits. See Section 14 for marginal exceedance criteria.

15.5.3 The RPD limits for MS/MSD must be ± 25%.

15.6 Method Blanks must be less than the reporting limits, with the exception of the following:

15.6.1 Phthalates are common laboratory contaminants and the presence contamination of these analytes in the method blank is common. If these analytes are found in the method blank (at concentrations less than five times the reporting limit), they may be reported to the client along with the sample results.

15.6.2 Client specific requirements may require that method blanks be evaluated to ½RL. In this case, any method blank that has a positive result >½ RL must be evaluated and the problem identified and corrected, or documented in the final report of the final report.

15.7 Corrective Actions for Out-of Control Data

15.7.1 Method blanks that have been contaminated with compounds of interest will be evaluated to determine the source of the contamination. When the evaluation has been completed and the source of the contamination has been identified and addressed, the corrective action may include:

15.7.1.1 Re-analysis of the sample extracts in the batch.

15.7.1.2 Re-extraction and reanalysis of some or all of the samples in the batch, with new QC samples. (provided there is enough sample available)

15.7.1.3 Documentation of any QC failures in the final report if there is insufficient sample for re-extraction or due to hold time issues.

15.7.2 Any surrogate, matrix spike or LCS recovery that is outside of the acceptance limit(s) require evaluation to determine the cause of the problem and may include but is not limited to:

15.7.2.1 Comparison of the surrogate and MS results to the LCS results to determine if there are matrix interferences resulting in the exceedence (e.g., high levels of background interferences or target analytes in the sample).

15.7.2.2 Evaluation of the instrument run conditions to determine if any changes have taken place that would result in the identified exceedence(s) (i.e., system sensitivity, chromatography, carryover).

15.7.2.3 Evaluation of the extraction and/or cleanup procedures to determine if there were any errors, problems or observations made by the prep analysts that would result in the exceedence(s) noted.

15.7.2.4 Evaluation of the standards and reagents used in the extraction and analysis to determine if any errors or problems have occurred that would result in the exceedence(s) noted. (i.e., spiking or concentration errors).

15.7.3 When the sample evaluation for any MS, surrogate or LCS recovery exceedance has been completed and the problem has been identified and addressed, the corrective action may include:

15.7.3.1 Re-analysis of the sample extracts in the batch.

15.7.3.2 Re-extraction and reanalysis of some or all of the samples in the batch with new QC samples (provided there is enough sample available).

15.7.3.3 Documentation of any QC failures in the final report if there is insufficient sample for re-extraction or due to hold time issues.

15.7.4 Samples with internal standard recoveries that are outside of the 50-200% (from the CCAL) range will be re-prepared using fresh aliquots of the extract and reanalyzed to determine if an error was made in the addition of the internal standard solution to the sample extract, if the internal standard solution has concentrated, or if there is matrix interference that affects the internal standard concentration. Otherwise, affected analytes will be flagged and no further corrective action will be taken.

15.8 Contingencies for Handling Out-of Control or Unacceptable Data

15.8.1 If reextraction of samples for unacceptable surrogate or spike recoveries is determined to be necessary, but is not possible due to insufficient sample amounts, the appropriate Project Manger will be notified to determine if additional sample may be obtained from the client. If this is not possible, the unacceptable recoveries, as well as the inability to reextract the sample due to insufficient sample volume will be noted in the final report accompanying the data report.

15.8.2 If the reextraction and reanalysis of the sample or QC sample fails to yield acceptable results it shall be noted in the final report of the data report. The Department Manager/Supervisor and analyst, based on their assessments of sample matrix effects present, will determine what further steps, if any, need to be taken, up to and including informing the appropriate Project Manager.

15.8.3 If reextraction of an unacceptable sample yields acceptable recoveries and was re-extracted within holding time, the second analysis will be reported.

15.8.4 If reextraction of an unacceptable sample yields acceptable recoveries and was not within holding time but does confirm the original sample results, the initial analysis will be reported. A note will be added to the final report stating that the re-extraction past hold yielded acceptable recoveries and confirmed the original results.

15.8.5 If reextraction of an unacceptable sample yields acceptable recoveries and was not within holding time but does not confirm the original results, the Project Manager will be contacted to discuss.

15.9 Table 11 summarized the calibration and QA/QC Requirements for method 8270D.

15.10 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.11 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.12 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

16.2 Spent sample extracts and solvent rinses are collected for disposal in labeled containers.

16.3 Spent solvents and extracts are collected for appropriate disposal according to current EPA waste regulations. Pipettes used for measuring pure materials such as these described shall be placed in a seal-able bag (e.g., Ziploc®, or equivalent). Label the bag with the name of the material and its purity and store for proper disposal by a licensed hazardous waste disposal company.

17. References

17.1 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.2 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.3 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.4 USEPA, SW-846 III Ed., Determinative Chromatographic Separations. Method 8000B. Revision 2. December 1996.

17.5 USEPA, SW-846, Determinative Chromatographic Separations. Method 8000C. Revision 3. March 2003.

17.6 USEPA, SW-846, Final Update IV, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, Feb 2007.

17.7 USEPA, SW-846 III Ed., Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Method 8270C, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), September 1986.

17.8 Contract Laboratory Program Statement of Work (SOW) for Multi-Media, Multi-Concentration Organics Analysis (SOM04.2).

17.9 SOPs PGH-O-028 Separatory Funnel Extraction, current version.

17.10 SOP PGH-O-022 Microwave Extraction, current version.

17.11 SOP PGH-O-007, Solid Phase Extraction, current version.

17.12 SOP PGH-O-011, Waste Dilution Extraction, current version.

17.13 SOP PGH-M-016, Percent Moisture, current version.

17.14 SOP PGH-M-003, TCLP ZHE, current version.

17.15 SOP PGH-M-034, SPLP ZHE, current version.

17.16 SOP PGH-C-026, Control Charts, current version.

17.17 SOP PGH-Q-030, Manual Integrations, current version.

17.18 SOP PGH-C-032, Support Equipment, current version.

17.19 SOP PGH-Q-035, MDL-LOD, current version.

17.20 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.21 SOP PGH-Q-038, Laboratory Equipment, current version.

17.22 SOP PGH-Q-039, Corrective Action, current version.

17.23 SOP PGH-Q-040, Audits, current version.

17.24 SOP S-ALL-Q-020, Training, current version.

17.25 SOP S-ALL-Q-028, Lab Track, current version.

17.26 SOP PGH-C-027, DI Water, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

Table 1 - Characteristic Ions

Table 2 - Spiking Compounds

Table 3 - DFTPP Key Ions and Ion Abundance Criteria 8270C

Table 3A - DFTPP Key Ions and Ion Abundance Criteria **8270D**

Table 4 - Calibration Check Compounds (CCCs)

Table 5 - Internal Standard Assignment

Table 6 - Surrogate Compounds and Recovery Limits

Table 7 - Target Analytes and Reporting Limits

Table 8 - Method 8270D Minimum Response Criteria

Table 9 - LCS/MS Control Limits – Water

Table 10 - LCS/MS Control Limits – Soil

Table 11 – Summary of Method 8270D Calibration and QA/QC Requirements

Figure 1 – DDT/Benzidine Tailing Factor Calculation

19. Instrument Maintenance/Preventative Maintenance

19.1 Daily instrument maintenance should include changing the inlet sleeve and the septum. Also, the rinse solvent reservoirs should be checked daily and filled as needed.

19.2 To minimize peak tailing and active sites, the inlet seal should be changed and approximately 2-3in should be clipped off of the capillary column as needed. On average, this needs to be performed about twice per week.

19.3 Other routine maintenance that should be performed as needed include replacing the syringe, replacing the column, switching filaments, and cleaning the source.

19.4 Other maintenance needs to be performed periodically as needed due to parts breaking or wearing out.

19.5 Record all instrument maintenance in the maintenance logbook.

20. Method Deviations

20.1 The concentrations of the parameters listed for the tune, ICAL and CCV standards are ten (10) times lower than those recommended in EPA Method 8270C and 8270D.

20.2 All surrogates and LCS/MS spike concentrations are ten times lower than those listed in the methods to match the ICAL/CCV standards adjustment.

20.3 Currently using a combination of the tuning criteria listed in CLP OLM04.2 (all ions except 365 and 442) and method 8270C (ions 365 and 442).

21. Revisions

Document Number	Reason for Change	Date
PGH-O-001-6	Section 2.4: added reference to the MDLs. Section 12.1: added prep SOP references. Table 7: added compounds that are currently on the TNI cert but were not in the SOP. 1. General: made editorial corrections. Added method 8270D Criteria and references throughout the SOP. 2. Added Section 2.3. 3. Section 8.2: extracts store at < -10 °C for 8270C and at 6 °C for method 8270D. 4. Section 10.2.6.1: Typically seven calibration standards are prepared at different concentrations. 5. Calibration: added 8270D criteria. 6. Section 11.2.4: and <2 for method 8270D. 7. Added Section 11.3.4 8. Added Section 11.3.5 Linearity of target analytes 9. Added Section 11.3.6: 8270D Minimum Response Factors and LLCCV. 10. Added Section 11.3.7: 8270D Low Level Standard Read back for linear curve fit only. 11. Added Section 11.3.10. Evaluation of Retention Times. 12. Added Section 11.3.11 8270D calibration criteria. 13. Added Sections 11.3.15.2 and 11.3.15.3, ICV criteria for 8270C and 8270D. 14. Added Section 11.4, Removal of points from calibration curve. 15. Added Section 11.5, Basic Elements of calibration review. 16. Added Section 11.6.5 8270D CCAL criteria. 17. Updated control limits for surrogates, Matrix spike and LCS. Updated the surrogates in Table 6 and added control limits and ME limits for LCS in Tables 9 & 10. 18. Added Section 14.5.1: The following criteria shall be used for determining the minimum number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a two (2) year period. 19. Added Sections 14.5.2-14.5.4 20. Added Section 14.6 Allowable Marginal Exeedances. 21. Added RPD limit of 25% in section 15.5.3. 22. Updated references to add method 8270D, Quality manual reference and TNI standard. 23. Updated Section 18. 24. Document Reformatted. 25. Section 11.3.7, added read back of the low calibration standard for the quadratic curve also. 26. Added SOP references.	14Jul2014

Document Number	Reason for Change	Date
PGH-O-001-7	1. Section2.2 added reference to solid prep method 3546. 2. Section 10.2.7 & 10.2.8 added surrogate and spike standard concentration. 3. Section 11.3.2 added: For 2nd order quadratic curve a minimum of 6 calibration standards is required. 4. Section 11.5.2 added: minimum of five calibration standards is required. For 2nd order quadratic curve a minimum of 6 calibration standards is required. 5. Added to section 11.6.7.6 & 14.4 added: A method blank will be analyzed after calibration standards and prior to field sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants interferences from the analytical system including glassware and reagents. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. 6. Updated SOP references. 7. Updated control limits for LCS/MS and surrogates.	15Jun2015
PGH-O-001-8	1. Separated the ICAL and Continuing calibration by method for 8270C and 8270D. Added Table 11- Method 8270D Calibration and QA/QC Requirements.	11Aug2015
PGH-O-001-9	1. Added 1,2,4,5-Tetrachlorobenzene and control limit to Tables 9 and 10.	19Aug2015

Table 1: CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time(min.)	Primary Ion	Secondary Ion(s)
N-Nitroso-dimethylamine	3.62	74	42,43
Pyridine	3.68	79	52,51,50
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d4 (IS)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
2-Chlorophenol-d4 (Surr)	6.81	132	68,66,134
1,2-Dichlorobenze	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	44,45,74
1,2-Dichlorobenzene-d4 (Surr)	7.39	152	150,115,78
Thiophenol (Benzenethiol)	7.42	110	66,109,84
Methyl methanesulfonate	7.48	80	79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,82,80
Bis(2-chloroethoxy) methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	79,95,109,140
Ethyl methanesulfonate	9.62	79	109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d8 (IS)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	155,127,81,109
Diethyl sulfate	11.37	139	45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	108,77,79,90
Hexachloropropene	12.45	213	211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272

Table 1 (continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	41,42,68,69
Acetophenone	12.67	105	71,51,120
4-Methylphenol	12.82	107	108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	107,77,51,79
3-Methylphenol	12.93	107	108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,55,56,41
1,4-Phenylenediamine	13.62	108	80,53,54,52
1-Chloronaphthalene	13.65[a]	162	27,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	76,50,148
Carbazole	14.90	167	166,139,168
o-Anisidine	15.00	108	80,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d10 (IS)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	164,126,98,63
4-Chloroaniline	15.50	127	129,65,92
Isosafrole	15.60	162	131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	104,102,76,50,130
p-Cresidine	16.45	122	94,137,77,93
Dichlorovos	16.48	109	185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	135,134,91,77
N-Nitrosodi-n-butylamine	16.73	84	57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	104,77,103,135
Caprolactum	--	113	55,56
1,1'-Biphenyl	--	154	153,76
Atrazine	--	200	173,215
Bezaldehyde	--	77	105,106

Table 1 (continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramide	17.33	135	44,179,92,42
3-(Chloromethyl)pyridine HCL	17.50	92	127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	214,179,108,143,218
1-Naphthylamine	18.20	143	115,89,63
1-Acetyl-2-thiourea	18.22	118	43,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,79,106,94
Thionazine	19.35	107	96,97,143,79,68
4-Nitroaniline	19.37	138	65,108,92,80,39
Phenanthrene-d10 (IS)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	75,50,76,92,122
Mevinphos	19.90	127	192,109,67,164
Naled	20.03	109	145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	76,50,75,92,122
Diallate (cis or trans)	20.57	86	234,43,70
1,2-Dinitrobenzene	20.58	168	50,63,74
Diallate (trans or cis)	20.78	86	234,43,70
Pentachlorobenzene	21.35	250	252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	79,52,138,153,77
Pentachloronitrobenzene	21.72	237	142,214,249,295,265
4-Nitroquinoline-l-oxide	21.73	174	101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	131,230,166,234,168
Dihydrosaffrole	22.42	135	64,77
Demeton-O	22.72	88	89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	74,213,120,91,63
Dicrotophos	23.82	127	67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	43,264,41,290
Bromoxynil	23.90	277	279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	192,67,97,109
Phorate	24.10	75	121,97,93,260

Table 1 (continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Sulfallate	24.23	188	88,72,60,44
Demeton-S	24.30	88	60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	93,125,143,229
Phenobarbital	24.70	204	117,232,146,161
Carbofuran	24.90	164	149,131,122
Octamethyl pyrophosphoramide	24.95	135	44,199,286,153,243
4-Aminobiphenyl	25.08	169	168,170,115
Dioxathion	25.25	97	125,270,153
Terbufos	25.35	231	57,97,153,103
a, a- Dimethylphenylamine	25.43	58	91,65,134,42
Pronamide	25.48	173	175,145,109,147
Aminoazobenzene	25.72	197	92,120,65,77
Dichlone	25.77	191	163,226,228,135,193
Dinoseb	25.83	211	163,147,117,240
Disulfoton	25.83	88	97,89,142,186
Fluchloralin	25.88	306	63,326,328,264,65
Mexacarbate	26.02	165	150,134,164,222
4,4'-Oxydianiline	26.08	200	108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	152,141,169,151
Phosphamidon	26.85	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	185,41,193,266
Methyl parathion	27.03	109	125,263,79,93
Carbaryl	27.17	144	115,116,201
Dimethylaminoazobenzene	27.50	225	120,77,105,148,42
Propylthiouracil	27.68	170	142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d12 (IS)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	125,127,93,158
Kepone	28.18	272	274,237,178,143,270
Fenthion	28.37	278	125,109,169,153
Parathion	28.40	109	97,291,139,155
Anilazine	28.47	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	106,196,180
Carbophenothion	28.58	157	97,121,342,159,199
5-Nitroacenaphthene	28.73	199	152,169,141,115
Methapyrilene	28.77	97	50,191,71
Isodrin	28.95	193	66,195,263,265,147

Table 1 (continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Captan	29.47	79	149,77,119,117
Chlorfenvinphos	29.53	267	269,323,325,295
Crotoxyphos	29.73	127	105,193,166
Phosmet	30.03	160	77,93,317,76
EPN	30.11	157	169,185,141,323
Tetrachlorvinphos	30.27	329	109,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	167,195
Barban	30.83	222	51,87,224,257,153
Aramite	30.92	185	191,319,334,197,321
Benzo(b)fiuoranthene	31.45	252	253,125
Nitrofen	31.48	283	285,202,139,253
Benzo(k)fiuoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	139,253,111,141
Fensulfothion	31.87	293	97,308,125,292
Ethion	32.08	231	97,153,125,121
Diethylstilbestrol	32.15	268	145,107,239,121,159
Famphur	32.67	218	25,93,109,217
Tri-p-tolyl phosphate[b]	32.75	368	367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d12 (IS)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	241,239,120
5,5-Diphenylhydantoin	33.40	180	104,252,223,209
Captafol	33.47	79	77,80,107
Dinocap	33.47	69	41,39
Methoxychlor	33.55	227	228,152,114,274,212
2-Acetylaminofiuorene	33.58	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	201,229
3-Methylcholanthrene	35.07	268	252,253,126,134,113
Phosalone	35.23	182	184,367,121,379
Azinphos-methyl	35.25	160	132,93,104,105
Leptophos	35.28	171	377,375,77,155,379
Mirex	35.43	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,119,217,219,199
Dibenz(a,j)acridine	36.40	279	280,277,250
Mestranol	36.48	277	310,174,147,242
Coumaphos	37.08	362	226,210,364,97,109
Indeno(1,2,3-cd) pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2,4,5-tetrachlorobenzene	41.60	302	151,150,300

Table 1 (continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	135,105,77
Hexachlorophene	47.98	196	198,209,211,406,408
Aldrin	--	66	263,220
Aroclor 1016	--	222	260 292
Aroclor 1221	--	190	224 260
Aroclor 1232	--	190	224 260
Aroclor 1242	--	222	256 292
Aroclor 1248	--	292	362 326
Aroclor 1254	--	292	362 326
Aroclor 1260	--	360	362 394
Alpha-BHC	--	183	181,109
Beta-BHC	--	181	183,109
Gamma-BHC	--	183	181,109
y-BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237.165
4,4'-DDE	--	246	248 176
4,4'-DDT	--	235	237 165
Dieldrin	--	79	263 279
1,2-Diphenylhydrazine	--	77	105 182
Endosulfan I	--	195	339 341
Endosulfan II	--	337	339 341
Endosulfan sulfate	--	272	387 422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr)	--	172	171
2-Fluorophenol (surr)	--	112	64
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d5 (surr)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d6 (surr)	--	99	42,71
Terphenyl-d14 (surr)	--	244	122,212
2,4,6-Tribromophenol (surr)	--	330	332,141
Toxaphene	--	159	231,233

IS =internal standard
surr = surrogate
a-Estimated retention times
b-Substitute for the non-specific mixture, tricresyl phosphate

Table 2: CLP Matrix Spike Compounds and PAHs

1,2,4-Trichlorobenzene
1,4-Dichlorobenzene
1-Methylnaphthalene
2,4-Dinitrotoluene
2-Methylnaphthalene
4-Chloro-3-methylphenol
4-Nitrophenol
Acenaphthene
Acenaphthylene
Anthracene
Benz[a]anthracene
Benzo[a]pyrene
Benzo[b]fluoranthene
Benzo[ghi]perylene
Benzo[k]fluoranthene
Chrysene
Dibenz[a,h]anthracene
Fluoranthene
Fluorene
Indeno[1,2,3-cd]pyrene
Naphthalene
N-Nitroso-di-n-propylamine
Pentachlorophenol
Phenanthrene
Phenol 2-Chlorophenol
Pyrene
Pyrene

*Client Specific Requirements: May require that all target compounds be spiked, even if multiple LCS/MS/MSD samples are needed.

TCLP Matrix Spike Compounds

1,4-Dichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4-Dinitrotoluene
Hexachlorobenzene
Hexachlorobutadiene
Hexachloroethane
Nitrobenzene
Pentachlorophenol
Pyridine
Total Cresol

Table 3 - DFTPP Key Ions and Ion Abundance Criteria **8270C**

Mass	Ion Abundance Criteria
51	30-80% of mass 198
68	< 2% of mass 69
69	Present
70	< 2% of mass 69
127	25-75% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	15-24% of mass 442

Tailing Analysis:
8270C: Pentachlorophenol ≤5 and Benzidine ≤3.

DDT Degradation %Breakdown analysis Summary for 8270C:

4,4-DDE ≤ 15%
4,4-DDD ≤ 15%
4,4-DDD + DDE ≤ 15%

Table 3A - DFTPP Key Ions and Ion Abundance Criteria **8270D**

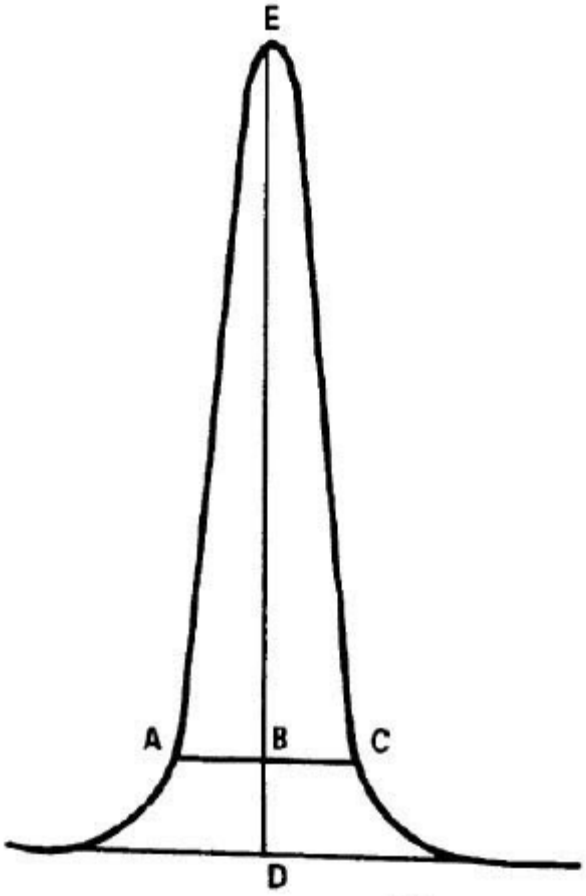
Mass	Ion Abundance Criteria
51	30-80% of mass 198
68	< 2% of mass 69
69	Present
70	< 2% of mass 69
127	25-75% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	15-24% of mass 442

Tailing Analysis:
8270D: Pentachlorophenol and Benzidine ≤2.

DDT Degradation %Breakdown analysis Summary for 8270D:

4,4-DDE ≤ 20%
4,4-DDD ≤ 20%
4,4-DDD + DDE ≤ 20%

Figure 1 - DDT/Benzidine Tailing Factor Calculation



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

Table 4 - Calibration Check Compounds (CCC) – 8270C

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

Table 5 - Semivolatile Internal Standards with Corresponding Analytes Assigned For Quantitation

1,4-Dichlorobenzene-d(4)	**Naphthalene-d(8)**	**Acenaphthene-d(1O)**
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	a,a-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d8(surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodibutylamine	2-Nitroaniline
Phenol-d6(surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
Benzaldehyde	Caprolactum	4-Nitrophenol
Acetophenone		Pentachlorobenzene
Acetophenone		1,2,4,5-Tetrachlorobenzene
2-chlorophenol-d4		2,3,4,6-Tetra-chlorophenol
1,2-Dichlorobenzene-d4		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol
		1,1'-Biphenyl

Table 5: (Continued)

Phenanthrene-d(10)	Chrysene-d(12)	Perylene-d(12)
4-Aminobiphenyl	Benzidine	Benzo(b)fluor-anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,I)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl-phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h) anthracene
Fluoranthene	p-Dimethylaminoazobenzene	Di-n-octylphthalate
Hexachlorobenzene	Pyrene	Ideno(1,2,3-cd) pyrene
N-Nitrosodiphenylamine	Terphenyl-d14(surr.)	
Pentachlorophenol	7,12-Dimethylbenz-(a)anthracene	
Pentachloronitrobenzene	3-Methylchol-anthrene	
Phenacetin		
Phenanthrene		
Pronamide		
2,4,6 Tribromophenol(surr.)		
Atrazine		
Carbazole		

(surr) = surrogate

Table 6 - Surrogate (DMCs) Recovery Limits

Compound	% Recovery Water	% Recovery Soil/Sediment
Nitrobenzene-d5 (Base/Neutral)	22-128	40-117
2-Fluorobiphenyl (Base/Neutral)	34-113	50-112
Terphenyl-d14	35-150	52-130
Phenol-d5 (Acid)	14-49	53-115
2-Fluorophenol	19-70	38-124
2,4,6-Tribromophenol (Acid)	34-134	21-133

Note: All control Limits are subject to change, the most current control limits are in the laboratory's LIMs.

Table 7 – Target Analytes and Reporting Limits

Analyte	RL Water (µg/L)	RL Low Level Water (µg/L)	RL Soil (µg/Kg)
1,1'Biphenyl *	10	1	333
1,2,4,5-Tetrachlorobenzene	10	1	333
1,2,4-Trichlorobenzene	10	1	333
1,2-Dichlorobenzene	10	1	333
1,2-Diphenylhydrazine	10	1	333
1,3-Dichlorobenzene	10	1	333
1,4-Dichlorobenzene	10	1	333
1,4-Dioxane *	NA	NA	NA
1-Methylnaphthalene *	10	1	333
2,3,4,6-Tetrachlorophenol	10	1	333
2,4,5-Trichlorophenol	25	2.5	833
2,4,6-Trichlorophenol	10	1	333
2,4-Dichlorophenol	10	1	333
2,4-Dimethylphenol	10	1	333
2,4-Dinitrophenol	25	2.5	833
2,4-Dinitrotoluene	10	1	333
2,6_Dinitrotoluene	10	1	333
2-Chloronaphthalene	10	1	333
2-Chlorophenol	10	1	333
2-Methylnaphthalene	10	1	333
2-Methylphenol	10	1	333
2-Nitroaniline	25	2.5	833
2-Nitrophenol	10	1	333
3&4 Methylphenol	20	2	666
3,3'-Dichlorobenzidine	10	1	333
3-Nitroaniline	25	2.5	833
4,6-Dinitro-2-methylphenol	25	2.5	833
4-Bromophenylphenylether	10	1	333
4-Chloro-3-methylphenol	10	1	333
4-Chloroaniline	10	1	333
4-Chlorophenylphenylether	10	1	333
4-Nitroaniline	25	2.5	833
4-Nitrophenol	10	1	833
8-Hydroxyquinoline *	10	NA	NA
Acenaphthene	10	1	333
Acenaphthylene	10	1	333
Acetophenone	10	1	333
Aniline	25	2.5	333
Anthracene	10	1	333
Atrazine *	10	1	333

Analyte	RL Water (µg/L)	RL Low Level Water (µg/L)	RL Soil (µg/Kg)
Azobenzene	10	1	333
Benzaldehyde *	10	1	333
Benzidine	100	100	3300
Benzo(a)anthracene	10	1	333
Benzo(a)pyrene	10	1	333
Benzo(b)fluoranthene	10	1	333
Benzo(g,h,i)perylene	10	1	333
Benzo(k)fluoranthene	10	1	333
Benzoic Acid	100	25	833
Benzyl Alcohol	10	1	333
Bis(2-chloroethoxy)methane	10	1	333
Bis(2-Chloroethyl)ether	10	1	333
Bis(2-Chloroisopropyl ether	10	1	333
Bis(2-ethylhexyl)phthalate	10	1	333
Butylbenzylphthalate	10	1	333
Caprolactam *	25	2.5	833
Carbazole *	10	1	333
Chrysene	10	1	333
Dibenz(a,h)anthracene	10	1	333
Dibenzofuran	10	1	333
Diethylphthalate	10	1	333
Dimethylphthalate	10	1	333
Di-n-butylphthalate	10	1	333
Di-n-octylphthalate	10	1	333
Fluoranthene	10	1	333
Fluorene	10	1	333
Hexachloro-1,3-butadiene	10	1	333
Hexachlorobenzene	10	1	333
Hexachlorocyclopentadiene	10	1	333
Hexachloroethane	10	1	333
Indeno(1,2,3-cd)pyrene	10	1	333
Isophorone	10	1	333
Naphthalene	10	1	333
Nitrobenzene	10	1	333
N-Nitrosodimethylamine	10	1	333
N-nitroso-di-n-propylamine	10	1	333
N-Nitrosodiphenylamine	10	1	333
Pentachlorophenol	25	2.5	833
Phenanthrene	10	1	333
Phenol	10	1	333
Pyrene	10	1	333
Pyridine *	25	1	833

Analyte	RL Water (µg/L)	RL Low Level Water (µg/L)	RL Soil (µg/Kg)
Tributyl phosphate *	10	NA	NA

Note: compounds denoted with an * are not listed in method 8270D and are therefore a method modification.

Table 8 - Method 8270D Minimum Response Factor Criteria

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800

Table 8 - Continued

Semivolatile Compounds	Minimum Response Factor (RF)
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

Table 8 - Continued

Semivolatile Compounds	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

Table 9 - 8270C and 8270D LCS and MS Control Limits - Water

Compound	LCL (%)	UCL (%)	LME (%)	UME (%)
1,2,4-Trichlorobenzene	37	99	27	109
1,2,4,5-Tetrachlorobenzene	10	175	--	--
1,2-Dichlorobenzene	31	112	17	125
1,3-Dichlorobenzene	29	108	15	121
1,4-Dichlorobenzene	34	91	24	101
1-Methylnaphthalene	46	107	35	117
2,4,5-Trichlorophenol	23	160	10	182
2.4.6-Trichlorophenol	51	127	39	139
2.4-Dichlorophenol	32	126	16	141
2,4-Dimethylphenol	30	124	14	139
2,4-Dinitrophenol	10	170	10	198
2,4-Dinitrotoluene	46	107	36	118
2,6-Dinitrotoluene	14	167	10	192
2-Chloronaphthalene	42	114	30	126
2-Chlorophenol	40	100	30	110
2-Methylnaphthalene	43	100	33	110
2-Methylphenol (o-cresol)	32	116	18	130
2-Nitroaniline	35	144	17	162
2-Nitrophenol	29	129	12	146
3,4-Methylphenol (mp-cresol)	30	103	18	115
3-Nitroaniline	20	163	10	186
4,6-Dinitro-2-methylphenol	20	154	10	176
4-Bromophenylphenyl ether	41	133	26	148
4-Chloro-3-Methylphenol	40	111	29	122
4-Chloroaniline	10	148	10	173
4-Chlorophenylphenyl ether	25	154	10	176
4-Nitroaniline	42	157	23	176
4-Nitrophenol	10	57	10	66
Acenaphthene	45	105	35	115
Acenaphthylene	45	106	35	116
Anthracene	54	107	46	115
Benzo(a)anthracene	68	106	61	112
Benzo(a)pyrene	60	108	52	116
Benzo(b)fluoranthene	63	120	54	130
Benzo(g,h,i)pyrelene	29	139	11	157
Benzo(k)fluoranthene	64	122	55	131
Benzyl Alcohol	16	121	10	139
Benzoic Acid	10	80	10	95
Butylbenzyl phthalate	40	153	21	172
Carbazole	51	142	35	157
Chrysene	69	103	71	108
Di-n-butyl phthalate	24	159	10	182
Di-n-octyl phthalate	40	148	22	166

Compound	LCL (%)	UCL (%)	LME (%)	UME (%)
Dibenz(a,h)anthracene	39	132	24	147
Dibenzofuran	46	127	32	141
Diethylphthalate	52	127	39	139
Dimethylphthalate	52	128	39	140
Fluoranthene	64	114	56	122
Fluorene	49	110	39	120
Hexachloro-1,3-butadiene	36	117	23	131
Hexachlorobenzene	53	128	40	141
Hexachlorocyclopentadiene	20	88	10	99
Hexachloroethane	26	110	12	124
Indeno(1,23-cd)pyrene	37	131	22	147
Isophorone	30	123	14	139
N-Nitroso-di-n-propylamine	41	110	30	122
N-Nitrosodimethylamine	13	90	10	103
N-Nitrosodiphenylamine	43	134	27	149
Naphthalene	45	101	36	111
Nitrobenzene	26	130	10	148
Pentachlorophenol	28	131	11	149
Phenanthrene	59	109	50	117
Phenol	15	46	10	51
Pyrene	53	115	43	126
bis(2-chloroethoxy)methane	36	129	20	145
bis(2-chloroethyl)ether	31	123	16	138
bis(2-chloroisopropyl)ether	28	124	12	140
bis(2-Ethylhexyl) phthalate	30	177	10	200
Biphenyl	10	175		
3,3'-Dichlorobenzidine	32	196		
8-Hydroxyquinoline	60	100		
Acetophenone	10	175		
Aniline	10	175		
Atrazine	10	175		
Acetophenone	10	175		
Azobenzene	34	136		
Benzaldehyde	10	175		
Benzidine	10	100		
Caprolactum	10	175		
Tributylphosphate	60	100		
Pyridine	10	175		
Note: ME limits only apply to LCS				

Note: All control Limits are subject to change, the most current control limits are in the laboratory's LIMs.

Table 10 - 8270C and 8270D LCS and MS Control Limits – Soil

Compound	LCL	UCL	LME	UME
1,2,4-Trichlorobenzene	53	107	44	116
1,2,4,5-Tetrachlorobenzene	10	175	--	--
1,2-Dichlorobenzene	50	127	37	140
1,3-Dichlorobenzene	48	125	35	138
1,4-Dichlorobenzene	61	105	53	112
1-Methylnaphthalene	10	175		
2,4,5-Trichlorophenol	67	136	55	148
2.4.6-Trichlorophenol	67	135	56	146
2.4-Dichlorophenol	37	133	21	149
2,4-Dimethylphenol	33	137	16	154
2,4-Dinitrophenol	10	160	10	185
2,4-Dinitrotoluene	73	119	65	127
2,6-Dinitrotoluene	23	169	10	193
2-Chloronaphthalene	63	124	53	135
2-Chlorophenol	70	110	63	117
2-Methylnaphthalene	55	111	46	120
2-Methylphenol (o-cresol)	61	129	49	140
2-Nitroaniline	75	136	64	147
2-Nitrophenol	36	134	15	151
3,4-Methylphenol (mp-cresol)	49	142	33	158
3-Nitroaniline	58	161	40	178
4,6-Dinitro-2-methylphenol	45	157	26	176
4-Bromophenylphenyl ether	68	133	57	143
4-Chloro-3-Methylphenol	58	115	49	125
4-Chloroaniline	12	147	10	170
4-Chlorophenylphenyl ether	69	127	59	137
4-Nitroaniline	25	195	10	200
4-Nitrophenol	56	145	41	160
Acenaphthene	74	109	68	115
Acenaphthylene	77	110	71	116
Anthracene	85	109	81	113
Benzo(a)anthracene	82	111	77	116
Benzo(a)pyrene	85	110	80	115
Benzo(b)fluoranthene	76	124	68	132
Benzo(g,h,i)pyrelene	30	156	10	177
Benzo(k)fluoranthene	74	125	65	133
Benzyl Alcohol	54	139	40	154
Benzoic Acid	11	128	10	147
Butylbenzyl phthalate	64	152	49	167
Carbazole	56	172	37	192
Chrysene	83	114	78	119
Di-n-butyl phthalate	73	127	64	136
Di-n-octyl phthalate	66	146	52	159
Dibenz(a,h)anthracene	44	146	27	163
Dibenzofuran	70	130	60	140

Compound	LCL	UCL	LME	UME
Diethylphthalate	70	128	61	138
Dimethylphthalate	67	126	58	136
Fluoranthene	82	115	77	120
Fluorene	79	112	74	117
Hexachloro-1,3-butadiene	34	138	17	155
Hexachlorobenzene	72	128	63	137
Hexachlorocyclopentadiene	32	116	18	130
Hexachloroethane	51	123	38	136
Indeno(1,2,3-cd)pyrene	42	146	25	163
Isophorone	40	122	26	136
N-Nitroso-di-n-propylamine	66	117	58	126
N-Nitrosodimethylamine	16	145	10	166
N-Nitrosodiphenylamine	70	137	59	148
Naphthalene	53	112	43	122
Nitrobenzene	31	131	14	148
Pentachlorophenol	18	150	10	172
Phenanthrene	84	109	79	113
Phenol	68	111	61	118
Pyrene	68	126	58	136
bis(2-chloroethoxy)methane	35	133	18	149
bis(2-chloroethyl)ether	50	125	37	137
bis(2-chloroisopropyl)ether	52	131	39	144
bis(2-Ethylhexyl) phthalate	68	145	55	158
2,3,4,6-Tetrachlorophenol	57	146	42	161
3,3'-Dichlorobenzidine	10	175		
Acetophenone	52	88	46	94
Aniline	10	175		
Atrazine	10	175		
Azobenzene	10	175		
Benzaldehyde	10	175		
Benzidine	10	175		
Biphenyl	10	175		
Caprolactum	10	175		
Pyridine	10	144	10	169
Note: ME limits only apply to LCS				

Note: All control Limits are subject to change, the most current control limits are in the laboratory's LIMs.

Table 11- Method 8270D Calibration and QA/QC Requirements					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Tune Check DFTPP	Prior to ICAL and prior to each 12-hour period of sample analysis	Specific ion abundance criteria of DFTPP, See SOP Section 11.2	Retune instrument and Verify. No samples shall be analyzed without a valid tune.	Flagging is not appropriate.	
Performance Check	At the beginning of each 12-hour period, prior to analysis of samples	Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol shall be present at their normal responses, and shall not exceed a tailing factor of 2. See SOP Section 11.2 & Table 3A.	Correct problem, then repeat performance checks	Flagging is not appropriate.	No samples shall be analyzed until performance check is within criteria. The DDT breakdown and Benzidine/Pentachlorophenol tailing factors are considered overall system checks to evaluate injector port inertness and column performance and are required regardless of the reported analyte list.
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up, prior to sample analysis	Each analyte must meet one of the three options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regression for each analyte: r ≥ 0.99; Option 3: non-linear least squares regression (quadratic) for each analyte: COD or r^2 ≥ 0.99. See SOP Section 15	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA	NA	

Table 11- Method 8270D Calibration and QA/QC Requirements					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Evaluation of Relative Retention Times (RRT)	With each sample	RRT of each reported analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within ± 30% of true value	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run	All reported analytes and surrogates within ± 20% of true value. See SOP section 20 for details.	If the % difference or drift is > 20%, corrective action must be taken prior to sample analysis. See SOP Section 11.10.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. See SOP section 11.10 for details.	
Internal standards (IS)	Every field sample, standard and QC sample	Retention time within ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within - 50% to +100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Flagging is not appropriate for failed standards.	
Method Blank (MB)	One per preparatory batch.	No analytes detected > RL or > ½ RL or > 1/10 the amount measured in any sample, whichever is greater. Common contaminants	Correct problem. If required, reprep and reanalyze MB and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s)	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 11- Method 8270D Calibration and QA/QC Requirements					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
		must not be detected > reporting limit.		in all samples in the associated preparatory batch.	
Laboratory Control Sample (LCS)	One per preparatory batch.	LCS limits listed in Table 9.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	Limits listed in Table 9.	If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error. See section 14.7 for details.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	Limits listed in Table 9.	If MSD or Duplicate results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error. See section 14.7 for details.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met and explain in the case narrative. See section 14.7 for details.	Must contain all surrogates and all analytes to be reported.
Surrogate Spike	All field and QC samples	Limits listed in Table 6.	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic	Apply flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	

Table 11- Method 8270D Calibration and QA/QC Requirements					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
			interference with surrogate is present, reanalysis may not be necessary.		

STANDARD OPERATING PROCEDURE

Polyaromatic Hydrocarbons by Selective Ion Monitoring
(PAHs by SIM)
EPA Method 8270C SIM & 8270D SIM

SOP NUMBER:	PGH-O-023-5
REVIEW:	Tim Harrison
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-O-023-4
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	6/9/14 Date
Senior Quality Manager	7/12/14 Date
Department Manager/Supervisor	7/9/14 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

TABLE OF CONTENTS

1. Purpose

1.1 This Standard Operating Procedure (SOP) documents the procedure used for the determination of polynuclear aromatic hydrocarbons (PAHs) in solids and liquids by gas chromatography/mass spectrometry by modified EPA Method 8270C and 8270D using Selective Ion Monitoring (SIM).

2. Scope and Application

2.1 This procedure is used to determine the concentration of PAHs in extracts prepared from all types of solid and aqueous matrices. Common target analytes and quantitation limits are shown in Table 1. Current MDLs are located in LIMS and are available from the Quality Department.

2.2 This procedure may not be used for other parameters until they have been fully developed and documented.

2.3 This procedure is based on EPA Methods 8270C and 8270D and uses Selective Ion Monitoring (SIM) to acquire the analytical data.

3. Summary of Method

3.1 Concentrated sample extracts are analyzed by a GC/MS system set up for SIM analysis. The qualitative identification of the analyte of interest in the extract is performed using the retention time and relative abundance of at least one characteristic mass. Quantitation is performed using the internal standard technique with a single characteristic mass in coordination with the calibration curve.

4. Interferences

4.1 Matrix interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the ion current profiles. All of these materials must be routinely demonstrated to be free from interferences by the analysis of laboratory reagent blanks.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the environment being sampled.

4.3 An interference that is unique to selected ion monitoring techniques can arise from the presence of an interfering compound containing the quantitation mass ion. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantitation ion and the confirmation ion are not within the specified limits, then interferences may be present.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Extract Storage – Semivolatile sample extracts shall be stored at a temperature of less than -10°C for method 8270C SIM and ≤ 6°C for method 8270D SIM,

protected from light, in sealed amber vials (e.g., crimp-capped vials) equipped with un-pierced PTFE-lined septa.

8.2 Samples extracts must be analyzed within 40 days of the sample extraction date.

9. Equipment and Supplies

9.1 Hewlett-Packard gas chromatograph/mass spectrometer model 5973/ 6890 and Hewlett-Packard Autosampler model 7683A, or equivalent.

9.2 Column: RTX-5MS, 20m x 0.18mm (ID) bonded-phase silicone coated fused silica capillary column, 0.18µm film thickness, or equivalent.

9.3 Carrier Gas: Helium

9.4 Data system for acquisition: An HP Chemstation® computer system or equivalent is interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration, of the chromatographic program. The computer is equipped with Target® or equivalent software that can search any GC/MS data file for ions of a specific mass and is capable of plotting such ion abundances versus time or scan number (EICP plot). The software allows integration of the abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also available on one or more operating systems in the Semivolatile laboratory

9.5 Recommended GC/MS operating conditions:

Dwell Time per ion:	30µS
Temperature Program:	70˚C, hold for 1.05 minutes
	70-210˚C at 40˚C/min
	210-230˚C at 30˚C/min
	230-345˚C at 25˚C/min hold for 2.68 min.
Injector Temperature:	270˚C
Transfer Line Temperature:	280˚C
Sample Volume:	0.5µL

10. Reagents and Standards

10.1 See the Semivolatile Standard Prep Logbook for the preparation of the standards listed in this SOP.

10.2 Initial Calibration (ICAL) standards: Purchased from Restek (or equivalent):

Standard 1 - 0.1mg/L

Standard 2 - 0.2mg/L

Standard 3 - 0.5mg/L

Standard 4 - 2.0mg/L

Standard 5 - 5.0mg/L

Standard 6 - 20.0mg/L

10.3 Continuing Calibration Verification (CCV) standard: Purchased from Restek (or equivalent) and prepared at 2.0mg/L.

10.4 Initial Calibration Verification (ICV) standard - All calibrations are verified using a second source standard.

11. Calibration

11.1 DFTPP

11.1.1 At the beginning of each analytical sequence, the GC/MS system is tuned using a 5.0mg/L injection of tuning mixture containing DFTPP, 4,4'-DDT, pentachlorophenol, and benzidine.

11.1.2 Analysis of initial calibration standards and samples shall not begin until the tuning criteria are met.

11.1.3 The mass spectrum needed to evaluate the success of DFTPP tuning is acquired as follows:

11.1.3.1 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

11.1.3.2 Background subtraction is required and accomplished using a single scan of no more than 20 scans prior to the elution of DFTPP. Background subtraction is designed only to eliminate column bleed or instrument background ions and must not subtract part of the DFTPP peak.

11.1.4 The ion abundances of the DFTPP standard are evaluated against the mass intensity criteria listed in Table 2.

11.1.4.1 Analysis may proceed if the ion abundances of the DFTPP standard are within the acceptance limits. System evaluation and maintenance may be required if the ion abundances are not within the specified limits.

11.1.5 Tailing factors for pentachlorophenol and benzidine and the breakdown of 4,4'-DDT are not evaluated for the SIM analysis.

11.2 INITIAL CALIBRATION (ICAL)

11.2.1 The mass spectrometer is operated in the selected ion monitoring (SIM) mode using the appropriate windows to include the quantitation and confirmation masses listed in Table 1.

11.2.2 Analytes are quantified using the internal standard with the closest retention time. If interferences are noted, use the next most intense ion as the quantitation ion.

11.2.3 Prior to the analysis of samples, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response utilizing calibration standards. The lowest level standard must be at or below the PQL. The midpoint calibration standard (CCV) should be used to establish retention time windows for each analyte.

Standard 1 - 0.1mg/L

Standard 2 - 0.2mg/L

Standard 3 - 0.5mg/L

Standard 4 - 2.0mg/L

Standard 5 - 5.0mg/L

Standard 6 - 20.0mg/L

11.2.4 Calculate response factors (RFs) for each compound.

11.2.5 Calculate the average RF for each compound and the percent relative standard deviation (%RSD).

11.2.5.1 The %RSD must be less than or equal to 15% for method 8270C SIM and less than or equal to 20% for method 8270D SIM for each compound or a different curve fit must be utilized.

11.2.5.2 The correlation coefficient (r) must be greater than or equal to 0.99 if a linear regression is used. The coefficient must be greater than or equal to 0.99 if a quadratic curve is used along with a minimum of 6 standard concentration levels.

11.2.5.3 For 2^{nd} order curves such as quadratic, the coefficient of determination (COD or r^2) $r^2 \geq 0.99$. 2^{nd} order curves should only be used in circumstances where a linear curve is clearly not appropriate. While quadratic curves are generally reliable within the calibration range, they can produce highly erroneous results above the calibration range including negative numbers at high concentrations. If a quadratic curve is used, each and every calibration plot must be visually inspected to ensure that the fitted function does not re-curve producing multiple concentrations for a single instrument signal.

11.2.6 Method 8270C SIM: All compounds must have an average response equal to or greater than 0.05.

11.2.7 Method 8270D SIM: Minimum response factors are listed in Table 5 for common target analytes.

11.2.8 Method 8270D SIM: If more than 10% of the compounds in the initial calibration exceed the 20% RSD or 0.990 correlation coefficient criteria, analysis cannot begin as the chromatographic system is considered too reactive. Perform maintenance and repeat the calibration procedure from the beginning.

11.3 **Removal of Points from a Calibration Curve:**

11.3.1 Removing or replacing of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. The curve is evaluated with the levels removed. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve must be reanalyzed. Corrective action may include instrument maintenance and/or repreparation of standards. If the low standard is dropped, then the lowest remaining calibration point must be at or below the reporting limit.

11.4 **Basic Elements of Calibration Review:**

11.4.1 The lowest calibration level must be at or below the RL. If this requirement is not met, the instrument must be recalibrated to include a lower concentration standard. The lowest calibration level must be higher than the MDL.

11.4.2 The minimum number of calibration points requirement must be met. If not, the instrument must be recalibrated.

11.4.3 Linearity requirements as stated in this SOP must be met. If this requirement is not met, the problem must be investigated, corrected, and the instrument recalibrated.

11.4.4 Examine the plots for quadratic fits: The calibration plots must be visually examined to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal.

11.5 Initial Calibration Verification (ICV)

11.5.1 The ICV must be prepared from source materials independent of the calibration standards. It must contain all target compounds in the calibration and meet the continuing calibration acceptance criteria. If the acceptance criteria are not met, the instrument must be recalibrated. Corrective actions may consist of performing maintenance or re-preparing the calibration standards if an error is suspected. The ICV is prepared at 2.0mg/L.

11.5.1.1 For 8270C SIM: Acceptance limits for the ICV are 80-120%. Target analytes failing the 20% criteria must be flagged as estimated values.

11.5.1.2 For 8270D SIM: Acceptance limits for the ICV are 70-130%. Target analytes failing the 30% criteria must be flagged as estimated values.

11.6 Continuing Calibration Verification (CCV)

11.6.1 A calibration standard containing each compound of interest must be analyzed every 12 hours. Compare the response factor data from the standards with the average response factor from the initial calibration for a specific instrument. The CCV is prepared at 2.0mg/L

11.6.2 Calculate the percent difference for each analyte.

11.6.2.1 The percent difference for each compound must be less than or equal to 20%. This criterion must be met before sample analysis proceeds.

11.6.2.2 The RF for each compound must be 0.050 or greater for method 8270C SIM and must be equal to or greater than the minimum RFs listed in Table 5 for method 8270D SIM. The internal standard responses and retention times in the calibration check standard must be evaluated after data acquisition.

11.6.2.3 If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard of the last ICAL, the analytical system must be inspected for malfunctions and corrections must be made.

11.6.3 If the area for any of the internal standards changes by a factor of two, (-50% to +100%) from the midpoint standard of the last ICAL, the system must be inspected for malfunctions and corrections must be made.

12. Procedure

12.1 GC/MS Analysis

12.1.1 The extract obtained from sample preparation is fortified with internal standard solution at 4mg/L. Sample preparation information can be found in SOPs PGH-O-028 (sep funnel extraction) and PGH-O-022 (microwave extraction).

12.1.2 The sample extracts are then analyzed by GC/MS system by injecting them onto the column.

12.1.3 If the response for any quantitation ion exceeds the initial calibration curve range, a dilution of the extract must be performed to bring the response into the upper half of the calibration range established.

12.1.3.1 Additional internal standard must be added to the diluted extract to maintain the required 4mg/L concentration.

12.1.4 Check all samples for adequate surrogate and internal standard recoveries after the twelve-hour sample run is completed. In addition, be sure that all samples contained in a particular run sequence have been analyzed within the 12-hour tune period. Reanalyze any that are outside the 12-hour tune period.

12.1.4.1 NOTE: All sample and QC surrogate recoveries are 'diluted out' at a 10x dilution.

12.1.5 Perform all qualitative and quantitative measurements as described in "Data Interpretation".

12.1.6 Samples may be analyzed upon successful completion of the initial calibration curve or successful continuing calibration verification standard for twelve (12) hours from the time of the tune standard injection.

12.1.7 Internal Standards Evaluation: Internal standard responses and retention times in all samples must be evaluated immediately after a run sequence or during data acquisition.

12.1.7.1 If the retention time for any internal standard changes by more than 30 seconds from the last CCV, then the analytical system must be inspected for malfunctions and corrections made as required.

12.1.7.2 If the area for any internal standard changes by more than a factor of two (-50% to 100%) from the latest daily calibration standard, the MS system must be inspected for malfunction and corrections made as appropriate.

12.1.8 Each analytical sequence must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds. If any compound in any sample exceeds the analytical range, that sample must be diluted, the internal standard concentration readjusted, and the sample re-injected, as described in specific methods.

12.2 Data Interpretation

12.2.1 Two criteria must be satisfied to verify the identification of any target analyte: 1) elution of the sample component at the same GC relative retention time as the standard component, and 2) correspondence of the sample component and standard component ion ratios.

12.2.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For comparison purposes, the RRT should be evaluated against the standard analyzed prior to the sample. See Table 1 for internal standard assignment.

12.2.3 Verification of the ion ratios for the samples must be performed against the ion ratios of the corresponding standard on the same GC/MS system.

12.2.4 Resolution between isomer pairs must be <25% of the sum of the two peak heights or the result must be reported as isometric pairs.

12.2.5 The relative intensities of ions must agree within ±20% between the standard and sample.

12.3 Manual Integrations: It is sometimes necessary for the analyst to perform manual integrations on samples or standards. This may be caused by sample matrix effects or limitations of the data processing software. The proper procedure for performing manual integrations can be found in the latest revision of SOP PGH-C-030.

13. Calculations

13.1 Quantitation is performed by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte (as assigned in Table 1).

13.1.1 The area of characteristic ions for each of the analytes listed in Table 1 is measured.

13.1.1.1 The secondary ions may be used in place of the primary ion if interferences are present.

13.1.1.2 The secondary ion cannot be substituted until the appropriate response factor has been calculated using the secondary ion.

13.2 Calculate the response factors (RFs) for each compound as follows:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg /mL).
C_x = Concentration of the compound being measured (µg /mL).

13.3 The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{SD}{\overline{RF}} x100$$

Where:

$\overline{RF}$ = Mean of the Response Factors mentioned above.
SD = Standard Deviation of initial response

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_1 - \overline{RF}\right)^2}{n-1}}$$

Where:

RF_1 = Each individual response factor
$\overline{RF}$ = Mean of the Response Factors mentioned above.
n = Number of response factors

13.4 The Percent Difference (%D) is calculated as follows:

$$\%Difference = \frac{\left(RF_i - RF_c\right)}{RF_i} x100$$

Where:

RF_i = Average response factor from initial calibration
RF_c = Response factor from current verification check standard

13.5 The concentration of analyte in the sample is calculated as follows:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF}_i)(W_o)(V_i)}$$

$$\text{Concentration } (\mu g/Kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF}_i)(W_s)(V_i)\left(\frac{100-M}{100}\right)}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard injected in nanograms (ng)
W_o = Volume of sample extracted in liters
V_i = Volume of extract injected (µL)
V_t = Volume of total extract (mL)
$\overline{RF}$ = Average response factor from initial calibration
W_s = Mass for soil in Kg
M = % Moisture

13.6 Calculate the Matrix Spike and Surrogate Percent Recovery as follows:

$$\%\,Recovery = \frac{SSR - SR}{SA} x100$$

Where:

SSR = Spike Sample Results
SR = Sample Result
SA = Spike Added from spiking mix

13.7 The relative percent differences (RPD) is calculated using the following equation:

$$RPD = \frac{|A - B|}{(A + B)/2} x100$$

Where:

RPD = Relative Percent Difference
A = First Sample Value
B = Second Sample Value (duplicate)

13.8 Equations, calculations and evaluation criteria for higher order curves (linear regression, quadratic) can be found in EPA Methods 8270C, 8270D and 8000. If these criteria are used for any parameter in the calibration curve, they must also be applied to all subsequent samples and standards.

14. Quality Control

14.1 Method Blank

14.1.1 The method blank (MB) associated with a specific set or group of samples must be analyzed on each GC/MS system used to analyze that specific group or set of samples.

14.1.2 A MB must not contain results for target analytes that are greater than the reporting limit (1/2 the reporting limit for client specific criteria).

14.1.2.1 A method blank with results above the reporting limit must be investigated to identify the source of the contamination and appropriate corrective measures must be taken and documented.

14.2 Laboratory Control Samples (LCS)

14.2.1 LCS results are used to verify that the precision and bias of the analytical process are within control. All target analytes are included in the spike solution. The results of the LCS are compared to the acceptance limits to determine usability of the data. Recovery limits for all compounds are listed in Table 4.

14.2.1.1 If target compound recoveries are not within the acceptance limits, the following actions are taken:

14.2.1.1.1 Check calculations to assure there are no errors; check internal standard and spiking solutions for degradation, contamination, etc., and check instrument performance.

14.2.1.1.2 Re-analyze the LCS if the step immediately above fails to reveal a problem. If reanalysis of the LCS solves the problem, then only the data from the analysis with spike recoveries within the acceptance limits will be submitted. If reanalysis of the LCS still results in recoveries outside acceptance limits, all samples should be reextracted and reanalyzed if possible.

14.2.1.1.3 If sample volume is available, reextract and reanalyze the samples associated with the LCS if the laboratory is unable to identify a definitive problem with the original extraction.

14.2.1.1.4 All deviations that cannot be corrected by the points listed above will be narrated in the final report.

14.2.1.2 Refer to the Marginal Exceedance section for LCS criteria.

14.3 Surrogate

14.3.1 Each sample is spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 3 are used to fortify each sample or blank with the proper concentrations. Performance based criteria are generated from laboratory results.

14.3.2 Surrogate spike recoveries must be evaluated for acceptance by determining whether the concentration (measured as % Recovery) falls inside the recovery limits established by the laboratory. Recovery limits for surrogates are listed in Table 3.

14.3.3 Sample Surrogate Recovery

14.3.3.1 When the surrogate recovery of any one surrogate compound is outside of the recovery limits, it is the responsibility of the laboratory to establish that the deviation is not due to laboratory problems.

14.3.3.2 The laboratory will document deviations outside acceptable Quality Control limits by taking the following actions:

14.3.3.2.1 Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc., and check instrument performance.

14.3.3.2.2 Reanalyze the sample if the step immediately above fails to reveal a problem. If reanalysis of the sample solves the problem, then only the sample data from the analysis with surrogate spike recoveries within the method windows will be submitted. Surrogate recoveries falling below 10 percent in a sample will require that the client be notified. The client will be advised that the sample should be reextracted and reanalyzed, or the results must be qualified with appropriate comments regarding the reason for the deficiency (i.e., matrix interferences). Discrepancy reports must be completed and routed as appropriate.

14.3.3.2.3 Reextract and reanalyze the sample if the laboratory is unable to identify a definitive problem with the original extraction.

14.3.3.2.4 Report the surrogate spike recovery data and the sample data from the original extraction.

14.3.3.2.5 All deviations that cannot be corrected by the points listed above will be narrated in a discrepancy report and the client notified.

14.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

14.4.1 One MS/MSD pair must be analyzed per preparation batch. If sufficient sample is not available to prepare an MS/MSD, it will be narrated in the final report.

14.4.2 All target compounds are used to prepare matrix spiking solutions. The analytical protocols require that a uniform amount of matrix spiking solution be added to the sample aliquots prior to extraction.

14.4.3 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

14.4.4 Calculate the percent recoveries and RPD for each parameter in the matrix spike. The recovery limits for all compounds are listed in Table 4. The acceptance limit for the RPD is 20%.

14.4.4.1 Matrix Spike Recovery: If the Matrix Spike recoveries do not meet the acceptance criteria, the batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed

and the spike recovery is not within the 20% RPD, a note is included in LIMS.

14.4.4.2 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.5 Spiking compounds for LCS and MS are listed in Table 4.

14.5.1 The following criteria shall be used for determining the minimum number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a two (2) year period:

14.5.2 For methods that include 1-10 targets, spike all components.

14.5.3 For methods that include 11-20 targets, spike at least ten (10) or 80%, whichever is greater.

14.5.4 For methods with >20 targets, spike at least 16 components.

14.6 **Allowable Marginal Exeedances**:

The LCS is spiked with the list of compounds listed in Tables 9 and 10. If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. This may not indicate that the system is out of control, therefore corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits are established to determine when corrective action is necessary. A ME is defined as being beyond the LCS control limit (three standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than eleven analytes.

14.6.1 The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
>90	5
71-90	4
51-70	3
31-50	2
11-30	1
<11	0

14.6.2 For methods 8270C and 8270D more than 90 compounds are spiked in the LCS, therefore the number of marginal exceedances allowed is five. The LCS control limits and the control limits for marginal exceedances are listed in Tables 9 and 10. **If more than 5 analytes exceed the LCS control limits and any one of the five compounds exceed the marginal exceedance limits, the LCS fails**.

14.6.3 If a LCS is spiked fewer than 90 compounds, the number of allowed marginal exceedances changes as listed in the table in Section 14.6.1.

14.6.4 If the same analyte exceeds the LCS control limit consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken. A lab track (corrective action database) ticket must be generated describing the failure, root cause, and corrective action.

15. Method Performance

15.1 There are several requirements that must be met to ensure that this procedure generates accurate and reliable data. A general outline of the requirements is summarized below. Further specifications may be found in the Quality Manual.

15.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

15.3 An initial demonstration of capability (IDC) must be performed and a record of the IDC maintained in the employee's training file.

15.4 A method detection limit (MDL) study will be completed, or verified, for this method annually or whenever there is a major change in equipment/sensitivity.

15.5 Periodic performance evaluation (PE) samples are analyzed to demonstrate continued competence.

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

16.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

16.3 The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner.

17. References

17.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Update I, Method 8270C

17.2 USEPA, SW-846, Final Update IV, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, Feb 2007.

17.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Update I, Method 8000B

17.4 USEPA, SW-846, Determinative Chromatographic Separations. Method 8000C. Revision 3. March 2003.

17.5 Contract Laboratory Program Statement of Work (SOW) for Multi-Media, Multi-Concentration Organics Analysis (SOM04.2).

17.6 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.7 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.8 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

Table 1: Analytes and Quantitation Limits

Table 2: DFTPP Tuning Criteria

Table 3: Surrogate Recovery Limits

Table 4: LCS/MS Recovery Limits

Table 5: Method 8270D Minimum Response Criteria

19. Instrument Maintenance

19.1 Daily instrument maintenance should include changing the inlet sleeve and the septum. Also, the rinse solvent reservoirs should be checked daily and filled as needed.

19.2 To minimize peak tailing and active sites, the inlet seal should be changed and approximately 2-3in. should be clipped off of the capillary column as needed. On average, this needs to be performed about once each week.

19.3 Other routine maintenance that should be performed as needed include replacing the syringe, replacing the column, switching filaments, and cleaning the source.

19.4 Other maintenance needs to be performed periodically as needed due to parts breaking or wearing out.

19.5 Record all instrument maintenance in the maintenance logbook.

20. Method Modifications

20.1 EPA Methods 8270C does not specifically detail the procedures to be followed for SIM Analysis. Due to the limited number of parameters being analyzed in this test, the following changes have been made:

20.1.1 The tune standard and calibration standards have concentrations that have been adjusted for low level analysis (lower concentrations).

20.1.2 The number of surrogates and internal standards has been reduced to just include base/neutrals.

20.1.3 Calibration of the system is only for the parameters of interest and do not include all of the CCC/SPCC compounds noted in method 8270C. As a result of this, all compounds being analyzed are considered CCC/SPCC compounds and must be treated accordingly for method 8270C.

20.1.4 Data acquisition is set up using SIM rather than full scan. Spectral matching of the standards and samples (as in full scan) is not possible. Reliance on retention times and ion ratio's is used for this procedure.

20.1.5 Currently using a combination of the tuning criteria listed in CLP OLM04.2 (all ions except 365 and 442) and method 8270C (ions 365 and 442).

21. Revisions

Document Number	Reason for Change	Date
PGH-O-023-5	1. Section 2.1: added comment regarding MDLs. 2. Section 2.3: removed unnecessary sentence. 3. Sections 11.6.2.3 and 11.6.3: corrected CCV internal language to match method. 4. Section 12.1.1: added prep SOP references. 5. Section 12.1.6.1: corrected sample internal language to match method. 6. Section 14.4.1: added frequency of MS/MSD. Added 8270D Criteria throughout the SOP 7. Added to section 8.1: Extract Storage – Semivolatile sample extracts shall be stored at less than -10°C for method 8270C SIM and 6°C or less for method 8270D SIM, protected from light, in sealed vials (e.g. crimp-capped vials) equipped with un-pierced PTFE-lined septa. 8. Section 11.1.5: Tailing factors for pentachlorophenol and benzidine and the breakdown of 4,4'-DDT are not evaluated for the SIM analysis. 9. Section 11.2.5.1 added 8270D SIM %RSD ≤ 20%. 10. Section 11.2.5.2 added: The correlation coefficient must be greater than or equal to 0.990 if a linear regression is used. The COD must be greater than or equal to 0.990 if a quadratic curve is used along with a minimum of 6 standard concentration levels. 11. Added Sections: 11.2.6: Method 8270C SIM: All compounds must have an average response equal to or greater than 0.05. 11.2.7: Method 8270D SIM: Minimum response factors are listed in Table 5 for common target analytes. 11.2.8: Method 8270D SIM: If more than 10% of the compounds in the initial calibration exceed the 20% RSD or 0.990 correlation coefficient criteria, analysis cannot begin as the chromatographic system is considered too reactive. Perform maintenance and repeat the calibration procedure from the beginning. 12. Added Section 11.3 Removal of points from a calibration curve. 13. Added Section 11.4 Basic Elements of Calibration Review. 14. Added Section 11.5.11 added ICV criteria for both methods. 15. Added Section 11.6.2.2: The RF for each compound must be 0.050 or greater for method 8270C SIM and must be equal to or greater than the minimum RFs listed in Table 5 for method 8270D SIM. The internal standard responses and retention times in the calibration check standard must be evaluated after data acquisition. 16. Added Section 14.2.1.2 – Refer to the marginal exceedance section for additional LCS criteria. 17. Added Section 14.5: Spiking compounds for LCS and ,S are listed in Table 4. 18. Added Section 14.6: Allowable marginal exceedances. 19. Updated references. 20. Updated surrogate and LCS/MS control limits added to the tables. Added Table 5: Min Response criteria for 8270D. 21. Moved revisions section to the end of the SOP. 22. Added SOP references.	01Jun2014

Table 1: Analytes and Quantitation Limits

PAH's	CAS Numbers	Quant	Ions Conf	Conf	Aqueous Reporting Limit (µg/L)	Solid Reporting Limit (µg/kg)
Napthalene-d8 IS	1520-96-3	135.9	136.9	108		
Naphthalene	91-20-3	128	127	136.9	0.1	6.7
1-Methylnaphthalene	90-12-0	142	141		0.1	6.7
2-Methylnaphthalene	91-57-6	142	141		0.1	6.7
Quinoline	91-22-5	129	102	103	0.1	6.7
Acenapthene-d10 IS	15067-26-2	164	162			
Acenaphthene	83-32-9	153	154	152	0.1	6.7
Acenaphthylene	208-96-8	152	151	153	0.1	6.7
Fluorene	96-73-7	166	165		0.1	6.7
2-Fluorobiphenyl Surr	321-60-8	172	171	170		
Phenanthrene-d10 IS	1517-22-2	188	93.9			
Phenanthrene	85-01-8	178.1	179		0.1	6.7
Anthracene	120-12-7	178.1	179.1		0.1	6.7
Fluoranthene	206-44-0	201.9	199.9	101	0.1	6.7
Chrysene	218-01-9	227.9	225.9	112.9	0.1	6.7
Chrysene-d12 IS	1719-03-5	240.1				
Benz(a)anthracene	56-55-3	227.9	225.9	113.9	0.1	6.7
Pyrene	129-00-0	201.9	199.9	101	0.1	6.7
Terphenyl-d14 Surr	98904-43-9	244.1	243.1	122		
Perylene-d12 IS	1520-96-3	264.2	265	132		
Benzo(a)pyrene	50-32-8	251.9	252.9	126	0.1	6.7
Benzo(b)fluoranthene	205-99-2	251.9	249.9	126	0.1	6.7
Benzo(k)fluoranthene	207-08-9	251.9	249.9	126	0.1	6.7
Indeno(1,2,3-cd)pyrene	193-39-5	275.9	137.9	136.9	0.1	6.7
Dibenz(a,h)anthracene	53-70-3	277.9	138.9	275.9	0.1	6.7
Benzo(g,h,i)perylene	191-24-2	275.9	137.9	136.9	0.1	6.7
1,4-Dichlorobenzene-d8 IS						
1,4-Dioxane	123-9-1				0.1	NA

IS = Internal Standard
Surr = Surrogate

Table 2: Ion Abundance Criteria For DFTPP

Mass (M/z)	Relative Abundance Criteria
51	30-80% of mass 198
68	< 2% of Mass 69
69	Present
70	< 2% of Mass 69
127	25-75% of mass 198
197	< 1% of Mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	15-24% of mass 442

Tailing and DDT degradation % breakdown analysis are not being evaluated for the SIM analysis.

Table 3: Surrogate %Recovery Limits (Lab-derived)

	Water		Soil	
Surrogate Compounds	**LCL (%)**	**UCL (%)**	**LCL (%)**	**UCL (%)**
2-Fluorobiphenyl	15	107	30	90
Terphenyl-d14	40	133	53	124

Table 4: LCS & Matrix Spike %Recovery Limits (Lab-derived)

	Water				Soil			
Compounds	**LCL (%)**	**UCL (%)**	**LME (%)**	**UME (%)**	**LCL (%)**	**UCL (%)**	**LME (%)**	**UME (%)**
1,4-Dioxane	10	40	10	48	NA	NA	NA	NA
1-Methylnaphthalene	10	175	10	175	10	175	10	NA
2-Methylnaphthalene	10	175	10	175	10	175	10	NA
Acenaphthene	41	119	27	133	57	100	50	108
Acenaphthylene	38	119	25	132	56	106	48	114
Anthracene	43	132	28	147	59	123	48	133
Benzo(a)anthracene	40	134	25	150	66	133	55	144
Benzo(a)pyrene	34	135	17	152	65	135	53	147
Benzo(b)fluoranthene	35	143	17	161	53	140	38	155
Benzo(g,h,i)pyrelene	23	149	10	170	57	132	44	145
Benzo(k)fluoranthene	39	152	20	171	65	153	51	168
Chrysene	40	141	23	158	66	146	52	159
Dibenz(a,h)anthracene	30	146	11	165	59	141	46	154
Fluoranthene	46	134	31	148	65	131	54	142
Fluorene	46	121	34	133	59	103	52	111
Indeno(1,2,3-cd)pyrene	32	152	12	172	60	134	48	146
Naphthalene	33	115	20	129	62	98	56	104
Quinoline	50	150			50	150		
Phenanthrene	36	124	22	138	59	107	51	115
Pyrene	45	132	30	146	65	123	56	133
Note: ME limits only apply to LCS								

Table 5: Method 8270D Minimum Response Criteria

Semivolatile Compounds	**Minimum Response Factor (RF)**
Naphthalene	0.700
2-Methylenaphthalene	0.400
Acenaphthylene	0.900
Acenaphthalene	0.900
Fluorene	0.900
Phenanthrene	0.700
Anthracene	0.700
Fluoranthene	0.600
Pyrene	0.600
Benzo(a)anthracene	0.800
Chrysene	0.700
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500

WORK INSTRUCTION FOR

Gasoline Range Organics (GRO)

Methods: EPA 8015B
Project Specific Requirement for Sparrow Point Project

SOP NUMBER:	WI-PGH-O-003-0
REVIEW:	Mike Klunk
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	Created from PGH-O-016-8
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager — 08/14/15 Date

Senior Quality Manager — 08/14/15 Date

Department Manager/Supervisor — 08/14/15 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

1. Purpose

   1.1 This SOP documents the procedure to be followed for the analysis of samples for Gasoline Range Organics (GRO) by EPA Method 8015B.

2. Scope and Application

   2.1 This procedure provides gas chromatographic conditions for the detection of alkanes ranging from C6 to C10 and covering a boiling point range of 60-170oC and may be used for both aqueous and solid samples.

   2.2 This method is restricted to use by, or under the supervision of analysts experienced in the operation of a purge and trap system, gas chromatography and the interpretation of GC data.

3. Summary of Method

   3.1 Samples are introduced into the gas chromatograph using a purge and trap system equipped with a capillary column which separates the compounds of interest into distinct peaks/patterns. These compounds are measured by a flame ionization detector (FID) placed at the end of the capillary column and the results for each sample are captured by a data acquisition system.

   3.2 See Table 2 for a listing of the reporting limits for aqueous and solid samples. Current MDLs are available from the Quality Department.

4. Interferences

   4.1 Major sources of contamination include solvent vapors in the laboratory, impurities in the nitrogen purging gas, and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) sealants, tubing, or flow controllers with rubber components is avoided, since such materials outgas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When contaminants are observed in the blanks, the purge gas source and/or the sorbent trap may need to be replaced.

   4.2 Samples may be contaminated by diffusion of volatile compounds through the septum seal during handling and storage. A trip blank prepared using organic-free (reagent) water and carried through the entire sampling, handling and storage procedures may be analyzed as part of the sample batch to determine contamination sources that may be outside the chromatographic system.

   4.3 Contamination may also occur when a sample containing low concentrations of VOCs is analyzed immediately after a sample containing high concentrations of volatile organic compounds VOCs. This is referred to as “carryover”. A technique to prevent this is to rinse with two portions of organic-free water between sample analyses. After the analysis of a sample containing high concentrations of VOCs, one or more blanks must be analyzed to check for carryover. If the sample analyzed immediately following the high concentration sample does not contain compounds present in the high level sample, freedom from contamination may be established.

5. Safety

   5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

   5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good

laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 GRO: Gasoline Range Organics

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Sample collection

8.1.1 Aqueous samples: At least two 40mL VOA vials should be filled and labeled immediately upon sample collection.

8.1.1.1 The vials must be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial inverted, no headspace is visible.

8.1.1.2 The sample must be hermetically sealed at the time of sampling, and must not be opened prior to analysis to preserve sample integrity. The presence of bubbles in a sample vial indicates either improper sampling technique or a source of gas evolution within the sample. In general, any bubbles less than 6mm in diameter will not adversely affect volatile data. If bubbles are observed to be larger than 6mm, the analyst must document this finding in the case narrative.

8.1.2 Waste and oil samples may be collected in 40mL VOA vials or any suitable glass container.

8.1.3 Soil samples: Refer to Pace Analytical SOP PGH-O-012 (Method 5035) for further information on the procedures to follow for solid sample collection.

8.1.4 There are several options available for collection and preservation of soil and aqueous sample. See Appendix 2 for details.

8.1.5 Refer to EPA Method 5035 & 5035A for further information.

8.2 Preservation

8.2.1 Aqueous samples are preserved with hydrochloric acid (HCl) to adjust the pH of the sample to <2.0. The VOA vials are purchased with hydrochloric acid added by the manufacturer C&G part number NC0152162, or equivalent.

8.2.1.1 pH preservation is checked in the Volatiles Department at the time of analysis.

8.2.2 Waste and oil samples do not require preservation. See Appendix 2 for details.

8.2.3 Soil samples: Refer to Pace Analytical SOP PGH-O-012 (Method 5035A) for further information on the procedures to follow for solid sample collection.

8.3 Shipment

8.3.1 Samples are checked for temperature upon receipt and should be received cooled to ≤6°C. Temperature readings outside this range will be documented in the project file.

8.4 Storage

8.4.1 Samples must be analyzed within 14 days of collection.

8.4.2 Samples are stored under refrigeration at ≤6°C from the time of receipt until 30 days after analysis.

9. Equipment and Supplies

9.1 Purge and Trap/Autosampler Device: O.I. Analytical 4552 water/soil Autosampler and a Tekmar 3000 Purge and Trap (or equivalent).

9.2 Gas Chromatograph: Hewlett Packard Model 5890, or equivalent, equipped with a flame ionization detector (FID).

9.3 Capillary Column: Restek RTX-VGS 30m, 0.53mmID column (or equivalent).

9.4 Sample containers: 40mL VOA vials with PTFE septa.

9.5 Data System: Chemstation®/Target® software. Used for operation of the GC system, acquisition of data and processing of GC information.

9.6 Balance: Mettler Model AE 240, capable of weighing to 0.0001g or equivalent.

9.7 Spatulas: Stainless Steel.

9.8 Syringes: Hamilton 10, 25, 50, 100, 250, 500 and 1000µL syringes. 5, 10, and 25mL gas-tight with shut off valve.

9.9 Glass Pipettes: Disposable 1.0mL and 10.0mL.

9.10 Volumetric Flasks: 5mL and 100mL, class A, glass.

9.11 pH paper – wide range.

9.12 VOA vials: I-CHEM 40mLglass container with a PTFE-lined septum and screw-cap.

9.13 Encore™ Sampler-field core sampling/storage container, or equivalent.

9.14 Ottawa sand-purified solid matrix, Fisher brand, or equivalent.

9.15 Repipette dispenser-Lab Industries, Inc., or equivalent.

10. Reagents and Standards

10.1 Methanol: Fisher Brand Purge and Trap grade, or equivalent.

10.2 Organic-free reagent water: Millipore Super Q (Milli-Q), or equivalent.

10.3 1.0mg/mL Gasoline Range Hydrocarbons Stock Solution: Restek brand, or equivalent.

10.4 WA VPH marker standard 100 µg/mL Restek brand, or equivalent.

10.5 100µg/mL Gasoline Range Hydrocarbons Working Solution: Dilute 1mL of 0.1µg/mL Gasoline Range Hydrocarbons Standard: Dilute 40µL of the 100µg/mL Gasoline Range Hydrocarbons Solution to 39.6mL Milli-Q water.

10.6 0.1µg/mL VPH marker standard. Dilute 1mL of 1.0mg/mL of WA VPH marker standard 100µg/mL to 10mL methanol.

10.7 2500µg/mL Unleaded Gasoline Composite (UGC) Standard: Restek brand, or equivalent.

10.8 Calibration curve solutions are prepared by adding the specified aliquots, in the table that follows, of 2500µg/mL Unleaded Gasoline Composite standard to approximately 95mL Milli-Q water in a 100mL volumetric flask. Once the standard has been added, dilute to volume with Milli-Q water. These initial calibration solutions (ICAL) may be kept in the refrigerator at ≤6°C

Std. Conc.	5000µg/mL	2000µg/mL	1000µg/mL	500µg/mL	200µg/mL
UGC Std	200µL	80µL	40µL	20µL	8µL

10.9 2500µg/mL 1-Chloro-4-Fluorobenzene Standard: Restek, brand or equivalent.

10.10 250µg/mL Internal Standard/Surrogate: Dilute 1mL 2500µg/mL 1-Chloro-4-fluorobenzene Standard to 10mL methanol.

10.11 2500µg/mL 4-Bromofluorobenzene Standard: Restek, brand or equivalent. (Surrogate).

10.12 250µg/mL Surrogate Standard: Dilute 1mL 2500µg/mL 4-Bromofluorobenzene & 1,1,1-Trifluorotoluene to 10mL methanol.

10.13 Continuing Calibration Standard (CCAL): Add 20µL of UGC Standard to 100mL Milli Q water.

10.14 NSI 5000µg/mL Laboratory Control Standard (LCS): Add 4µL of UGC Standard (different lot from the curve) to 40mL Milli-Q water in a 40mL vial.

10.15 NSI 5000µg/mL Matrix Spike Standards (MS/MSD): Add 4µL of UGC Standard (different lot from the curve) to 40mL vial of sample.

11. Calibration

11.1 Retention Time Verification: The 0.1µg/mL Gasoline Range Hydrocarbons standard is introduced by the purge and trap method. The chromatogram acquired from the system software is reviewed and the retention time windows are updated to include 2-methyl pentane through 1,2,4-trimethylbenzene as Gasoline Range Organics. The 0.1µg/mL VPH marker is introduced by the purge and trap method. The chromatogram acquired from the system software is reviewed and the retention time windows are updated for each of the carbon ranges.

11.1.1 Retention time windows are used to identify the target range in sample and standard chromatograms. Analyst experience should weigh heavily in the use of retention time windows and the identification of target ranges. See the procedure described in Appendix No. 1 of this SOP for the determination and setting of retention time windows.

11.2 Calibration standards are analyzed from lowest to highest concentration. A minimum of five calibration points are analyzed for a linear curve and six standards for 2nd order quadratic calibration curve. The resulting chromatograms are stored in the data system along with the quantity of standard corresponding to each calibration chromatogram.

11.2.1 The response factor (RF) is calculated for each calibration standard by the system software.

11.2.2 The average response factor, standard deviation and percent relative standard deviation (%RSD) is calculated.

11.2.3 The %RSD for the curve must be <20%.

11.3 The initial calibration verification standard (ICV from second source) must be within ±15% of the initial calibration response.

11.4 The continuing calibration verification (CCV) standards must have a percent difference that is within +15% of the initial calibration response.

11.5 Removal of Points from a Calibration Curve:

11.5.1 Removing or replacing of points from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. The curve is evaluated with the levels removed. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve must be

reanalyzed. Corrective action may include instrument maintenance and/or repreparation of standards. If the low standard is dropped, then the lowest remaining calibration point must be at or below the reporting limit.

11.6 Basic Elements of Calibration Review:

11.6.1 The lowest calibration level must be at or below the reporting limit (RL). If this requirement is not met the instrument must be recalibrated to include a lower concentration standard. The lowest calibration level must be higher than the Method Detection Limit (MDL).

11.6.2 The minimum number of calibration points requirement must be met. A minimum of five calibration standards is required. For 2nd order quadratic curve a minimum of 6 calibration standards is required. If not, the instrument must be recalibrated.

11.6.3 Linearity requirements as stated in this SOP must be met. If this requirement is not met, the problem must be investigated, fixed and the instrument recalibrated.

11.6.4 Examine the plots for quadratic fit: The calibration plots must be visually examined to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal.

11.6.5 Y-intercept – should be < ½ RL when reporting to the RL and <MDL when reporting to the MDL.

11.6.6 Increasing Response with Increasing Concentration: The instrument signal should increase with every increase in standard concentration.

12. Procedure

12.1 Equivalent amounts of the 250μg/mL internal standard and surrogate standards are added to the autosampler's standard reservoirs.

12.2 Sample Preparation:

12.2.1 Aqueous Samples: Samples are analyzed by placing the 40mL sample vial on the autosampler. The autosampler syringe on the removes a 5mL aliquot of the sample from the VOA vial and transfers it to the purge chamber. During this process, the autosampler is programmed to add 1μL of internal/surrogate standard into the 5mL aliquot of sample prior to purging. The sample is then purged and analyzed.

12.2.1.1 Water Dilutions: If the concentration of any target compound exceeds the initial calibration range, a new aliquot of sample must be diluted and analyzed. Additional dilutions may be necessary for extremely high concentrations. Calculate the volume of reagent water to be used and inject the appropriate volume of sample into the water. Cap the vial or flask and invert three times. The dilution is then placed onto the autosampler and analyzed.

12.2.2 Soil Samples: Samples are prepped following the procedure for medium level samples in Method 5035A. A dilution factor of 50 is analyzed. If results are less than the reporting limit, the value is reported as non-detect.

12.3 Once the samples have been analyzed, a report is generated by the Target® software or equivalent. This report shows the RT, the expected RT, the response,

the on column concentration, the final concentration, the internal area and RT summary, and the surrogate recovery report.

12.3.1 GRO is integrated from just before the 2-methylpentane peak to just after the 1,2,4-trimethylbenzene peak in the Gasoline Hydrocarbon Standard.

12.3.2 Baseline integration is to be preformed.

12.3.3 Peak area/height for the surrogates is not included in the GRO peak area.

12.4 Following analysis, the remaining sample in the VOA vial is used to check the pH with wide range pH paper and the pH of the sample is recorded in the analytical logbook. If the pH is greater than 2, this information is documented in the project final report accompanying the data.

12.5 Each instrument has a logbook in which all analyses performed including blanks, standards, client samples and QC samples are recorded. Other information documented includes analyst initial, date of analysis, sample identification, dilution factor, injection volume, and instrument identification and analysis numbers. A new folder containing standard and QC data is created each day and dated.

12.6 Individual project files contain all raw sample and applicable QC data. Copies of the ICAL, CCAL, and QC data are maintained within the Volatiles Department in folders according to the instrument identification and date of analysis.

13. Calculations

13.1 Water Samples:

$$\text{Concentration } (\mu g/L) = \frac{(Ax)\,(Is)\,(df)}{(Ais)\,(RRF)\,(Vo)}$$

Where:

Ax= Area of compound to be measured
Ais= Area of internal standard
Is= Amount of internal standard added, in nanograms (ng)
RRF= Relative response factor from the CCAL, for a specific compound
Df = Dilution factor
V_o= Volume of water purged, in milliliters (mL)

13.2 Soil Samples:

$$\text{Concentration } (\mu g/Kg) = \frac{(Ax)\,(Is)\,(Vt)\,(1000)\,(Df)}{(Ais)\,(RRF)\,(Ws)\,(D)\,(Va)}$$

Where:

Ax= Area of the compound to be measured
Ais= Area of internal standard
Is= Amount of internal standard added, in nanograms (ng)
RRF= Relative response factor from the CCAL, for a specific compound
Ws= Weight of sample analyzed, in grams (g)
D= (100-%moisture)/100
Vt= Total volume of the methanol extract, in milliliters (mL)
Va= Volume of aliquot taken from methanol extract in microliters (μL)

$RF = (A_s x C_{is})/)/ (A_{is} x C_s)$

Where:

A_s = Peak area of the analyte or surrogate
A_{is} = Peak area of the internal standard
C_s = Concentration of the analyte or surrogate
C_{is} = Concentration of the internal standard

13.3 Average RFs are calculated for each compound using the equation:

Σ *individual RFs / number of standards*

13.4 Using the five calibration standards, the system software will calculate the percent relative standard deviation (%RSD) for each compound using the following equation:

$%RSD = (RF_{SD} x 100)/ RF_{avg}$
Where:
RF_{SD} = the standard deviation of the five RFs for each compound
RF_{avg} = the average of the five RFs for each compound

8.1 Matrix Spike/ Duplicate, and LCS

$$\% \text{ Recovery} = \frac{C_{ss} - C_s}{S} \times 100$$

Where:

Cs = Concentration of the source sample
Css = Concentration of the spiked sample
S = Amount spiked

$$RPD = \frac{/(R_{MS} - R_{MSD})/}{(1/2)(R_{MS} + R_{MSD})} \times 100$$

Where:

RMS = Matrix Spike recovery
RMSD = Matrix Spike Duplicate recovery

14. Quality Control

14.1 A CCV (continuing calibration verification) is analyzed at the beginning and at the end of each analytical run. The CCV must be analyzed every 10 samples. The CCV must have a percent difference that is within +15% for 8015B. If the CCV is recovers high and samples are non-detect, samples can be reported with qualification. If the CCV recovers low, sample must be reanalyzed under a valid CCV. If there insufficient sample remaining for reanalysis, qualify the data.

14.2 A method blank, LCS and MS/MSD must be analyzed with each analytical batch or every twenty samples.

14.2.1 For aqueous samples, use Milli-Q water for method blank

14.2.2 For solid samples, use 0.8mL of 1:1 methanol: Ottawa sand and 40mL of Milli-Q water minus 8μL for method blank.

14.2.3 The method blank must be analyzed after the ICAL or CCAL but before any samples.

14.2.4 The result for the method blank must be less than the reporting limit (currently 200µg/L).

14.2.4.1 If the blank contains analytes of interest, a second blank may be analyzed to confirm sample contamination. If the second blank fails, sample analysis must desist until the system is cleaned and an acceptable blank has been analyzed.

14.2.4.2 Client specific requirements may require method blanks to be evaluated to ½ the RL.

14.2.4.3 Method blanks that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis evaluate the usefulness of the data in the final report.

14.3 Laboratory Control Sample (LCS): Include one LCS with each batch of up to 20 samples of the same matrix processed together. Percent recoveries for the LCS must fall within the laboratory-generated acceptance criteria listed in Table 3.

14.3.1 If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.3.2 When the acceptance criteria for the LCS are exceeded high (i.e., high bias) and there are associated samples that are non-detects, then those non-detects may be reported with data qualifying codes.

14.3.3 When the acceptance criteria for LCS compounds are exceeded low (i.e., low bias), those samples associated with the unacceptable LCS result must be reprepared and reanalyzed along with acceptable LCS.

14.4 MS and MSD samples are analyzed with each batch of samples unless there are is insufficient sample provided, in which case, only an LCS analyzed and a case narrative indicating insufficient sample for the MS/MSD is added to the final report.

14.4.1 Percent recoveries for MS samples must be within the limits found in Table 3.

14.4.2 If matrix spike recoveries are out of control, but the LCS sample results are acceptable, then it can be assumed that the unacceptable MS data are attributable to matrix effects. If MS/MSD recoveries are acceptable, but the RPD is out of control and reanalysis yields similar results, then it can be assumed that the sample matrix is adversely affecting the precision of test.

14.4.3 If the Matrix Spike recoveries do not meet the acceptance criteria, the batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported, and the results noted in the final report.

14.4.4 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.4.5 If there is no additional sample available for reanalysis evaluate the usefulness of the data in the final report.

14.5 Internal Standard: Evaluate the peak area and retention time for the internal standard in each analysis. The peak area for the standard must be >50% and <200% of the respective internal standard peak area in the most recent calibration verification standard. GRO internal standard acceptance criteria of 70-130% is used as per client specific requirement. If the peak area recoveries or retention times are outside these limits, perform the following procedures:

14.5.1 Check the standard to ensure proper preparation and that concentration has not occurred. If problems are identified, prepare new standards and reanalyze the samples.

14.5.2 Check to be sure that there are no errors in the calculations. If errors are identified, recalculate the data accordingly.

14.5.3 Check instrument performance. If a problem is identified, such as standard degradation or internal standard retention time shift, correct the problem and reanalyze the sample(s).

14.5.4 Some samples may contain peaks that interfere with the elution of the internal standard (matrix interference). In some instances, sample interferences may be so extreme that the sample must be diluted in order to achieve adequate quantitation of internal standards and target analytes. If sample dilution is required due to matrix effect, documentation of this must be included in the project final report.

14.5.5 If internal standard recoveries or retention times are outside the acceptance limits, reanalysis of the affected samples is required.

14.5.5.1 If, upon reanalysis, the recoveries or retention times are outside the limits, report the results of the original analysis and document the matrix interference in the project final report. If the recoveries or retention times are within limits for the second analysis and the sample was reanalyzed within the recommended holding time, report the results of the second analysis and document this in the project final report. If holding time has expired prior to reanalysis, consult with the Project Manager and Department Manager/ Supervisor in order to determine which results are to be reported.

14.5.5.2 If internal standard recoveries or retention times are outside the acceptance criteria in the sample and the MS/MSD, then matrix interference is assumed.

14.6 Surrogate recoveries must be within the limits found in Table 3. If the surrogate recoveries are not within limits, then perform the following procedures:

14.6.1 Check the standards to ensure proper preparation and that concentration or degradation has not occurred. If problems are found, re-prep standards and reanalyze samples.

14.6.2 Check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly.

14.6.3 Check instrument performance. If a problem is identified, correct the problem and reanalyze the sample(s).

14.6.4 Some samples may contain peaks that interfere with the elution of the surrogate standards (matrix interference). In some instances, sample interferences may be so extreme, that the sample must be diluted in order to achieve adequate quantitation of surrogates and analytes. If

sample dilution is required due to matrix effect, documentation of dilution due to matrix must be included in the final report.

14.6.5 If surrogates are below QC limits, reanalysis is required. If, upon reanalysis, the recoveries are again below QC limits, provide both result in project file and place a comment in the final report. If the recoveries are within limits in the reanalysis and the sample was reanalyzed within holding time, report only the reanalysis. If the holding time has expired prior to reanalysis, provide both result in project file, discuss situation with Project Manager, determine reportable data and include the comment in the final report. If surrogate recoveries are above QC limits and the results for the compounds of interest are below the reporting limits, the data may be reported with a comment in the final report.

15. Method Performance

15.1 The instrument must meet all the criteria for calibration and standardization (see Section 11).

15.2 Method performance is achieved through the analysis of annual MDLs, demonstration of capability (DOC) tests (annual and/or Performance Evaluation samples) and in-house laboratory Quality Control samples.

15.3 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.4 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.5 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC)

16. Pollution Prevention and Waste Management

16.1 All sample preparation involving the use of organic solvents (methanol, for example) is performed in a fume hood.

16.2 Sample solvent extracts and solvent rinses are collected in appropriately labeled containers.

17. References

17.1 USEPA, Method 5030C, Revision 3, May 2003, Purge-and-trap for aqueous samples.

17.2 USEPA, Method 5035A, Draft Revision 1, July 2002, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples.

17.3 USEPA, SW-846, Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

17.4 USEPA, SW-846, Third Ed., Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

17.5 USEPA, SW-846 III Ed., Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Methods 8015B, Revision 2, December 1996.

17.6 Total petroleum hydrocarbons (TPH) as Gasoline and Diesel, SW-846 Method 8015B (Revision 2, December 1996) EPA Addendum Tables.

17.7 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.8 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.9 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.10 SOP PGH-M-016, Percent Moisture, current version.

17.11 SOP PGH-C-026, Control Charts, current version.

17.12 SOP PGH-Q-030, Manual Integrations, current version.

17.13 SOP PGH-C-032, Support Equipment, current version.

17.14 SOP PGH-Q-035, MDL-LOD, current version.

17.15 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.16 SOP PGH-Q-038, Laboratory Equipment, current version.

17.17 SOP PGH-Q-040, Audits, current version.

17.18 SOP PGH-Q-039, Corrective Action, current version.

17.19 SOP S-ALL-Q-020, Training, current version.

17.20 SOP S-ALL-Q-028, Lab Track, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Table 1: Guidelines for GC operating conditions.

18.2 Table 2: Gasoline Range Organics Reporting Limits.

18.3 Table 3: LCS/MS Control Limits

18.4 Table 4: Surrogate Control Limits.

18.5 Attachment No. 1: Instrument Logbook Example.

18.6 Attachment No. 2: GRO Hydrocarbons Calibration Chromatogram Example.

18.7 Attachment No. 3: LCS Recovery Spreadsheet.

18.8 Appendix 1: Retention Time Determination.

18.9 Appendix 2: Recommended VOC Sample Preservation Techniques and Holding Times

19. Method Modifications

19.1 Method 8015 is only modified in order to follow state specific GRO ranges.

20. Revisions

Document Number	Reason for Change	Date
WI-PGH-O-002-0	1. Created project specific work instruction using the PGH-O-004 for the Sparrows Point project to add the requirements of Table 3 from 8015B Addendum Rev.2 Dec 1996. 2. In this work instruction Table 3 limits for LCS and MS were updated. Table 4 was added for surrogate limits for water and solid matrices. Additional surrogate compound added: 1,1,1-trifluorotoluene.	14Aug2015

Table 1 - Guidelines for GC Operating Conditions

Instrument Operating Conditions

Purge and Trap

Purge Gas	Nitrogen
Purge Time	8.0 Minutes
Purge Flow Rate	40mL/min
Purge Temperature	Ambient for waters or medium level soils (methanol extractions), and 40°C for low-level soil samples.
Desorb Temperature	250°C
Desorb Time	1 minute
Bake Temperature	260°C
Bake Time	5.0 minutes

Gas Chromatograph

Carrier Gas	Hydrogen
Initial Temperature	45°C
Initial Hold Time	3.0 minute
Ramp Rate	10°C/minute
Hold Temp	105°C
Hold Time	0 minutes
Ramp Rate	30°C/minute
Final Temperature	213°C
Injection Port Temp	250°C

Table 2 - Gasoline Range Organics Reporting Limits

Hydrocarbon Range	Water (µg/L)	Soil (mg/Kg)
Gasoline Range Organics	200	10
C6-C12	200	10
C6-C10	200	10
C5-C12	200	10
C5-C10	200	10

Note: Typical reporting limits for the parameters in this method. Additional Carbon Ranges or reporting limits may be developed to satisfy customer or agency requirements.

Table 3 - GRO LCS and Matrix Spike % Recovery Control Limits

	LCS % Recovery	Matrix Spike % Recovery	
Parameter	Water (%)	Solid (%)	Water/Soil RPD (%)
C6-C10	80-120	65-135	30
C6-C12	80-120	65-135	30

Table 4 - GRO Surrogate % Recovery Control Limits

Surrogate	Water	Solid
4-Bromofluorobenzene	75-125	60-125
1,1,1-Trifluorotoluene	75-125	60-125

Attachment No. 1 - Instrument Logbook (Example)

Doc#:VO002-0

Pace Analytical Services, Inc.-PGH
GC Volatile Analytical Run Logbook

Analyst	Date	Data file I.D.	Vial	Project #	Sample Identification	Soil Wt. (g)or Vol	DF	SF	pH	Cl	Comments
ESC	8/25/07	1			H_2O						
		2			GRO CCal						V2-61-1
		3			Blk						
		4-5			GRO LCS						V2-47-1
		6			MeOH Blk		5	5 8/25/07			
		7		6397	2934				<2		
		8		6414	3042		20				Orig Sample pH was Neutral
		9			3						
		10			4		5				Orig sample pH <2
		11			5						
		12			6						
		13		↓	7						
		14		6418	3065		10				Orig sample pH<2
		15			6						
		16			7						
		17		↓	8				↓		
		18		6489	3515				<2		
		19			6						
		20		↓	7				↓		
		21			H_2O						
		22		6489	3512	4.90	50	1.02			51
		23			3	5.39		0.923 8/24/07			46
		24		↓	4	4.51	↓	1.10			55
		25			H_2O						
↓	↓	26-27			GRO CCal						

Q:\Master\Document Management\VOA\GC VOA run Logbook (VO002-0 4Oct 2006)
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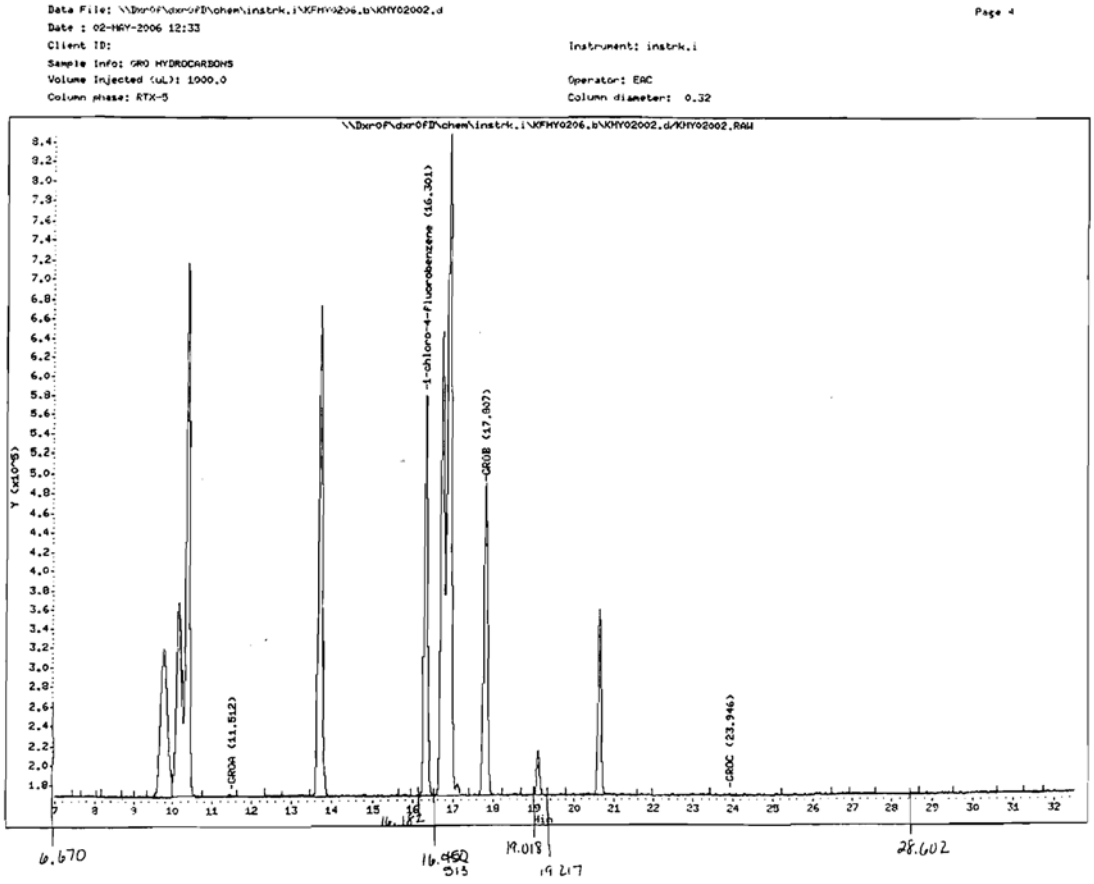
Peer Review_____

Attachment No. 2 - GRO Calibration Chromatogram (Example)



Attachment No. 3 - LCS Recovery Spreadsheet (Example)

GRO (8015) LCS/LCS DUPLICATE RECOVERY

Lab Name : Pace Analytical Services, Inc.

Project # : 05-0362

LCS # : 1

Date : 01/25/05

COMPOUND	Spike Added (µg/ml)	Method Blank Concentration (µg/ml)	LCS Concentration (µg/ml)	LCS % Rec	#	LCSD Concentration (µg/ml)	LCSD % Rec	#	% RPD	#	QC LIMITS % RPD & RECOVERY	
GRO	0.500	0.000	0.363	72.6		0.350	70.0		4		25	70 - 130

Spike Recovery Formula : ((LCS CONCN. - SAMPLE CONCN.) / (SPIKE ADDED)) * 100

Duplicate Recovery Formula : ((ABS(LCS REC. - LCSD REC.)) / ((LCS REC. + LCSD REC.) / 2)) * 100

Column: Used to flag recovery and RPD values.
* = Values outside of QC limits

Comments :

Appendix No. 1 - Determination of Retention Time Windows
EPA Method 8000C (Section 11.6)

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC and HPLC methods that do *not* employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

The following subsections describe one approach that may be used to establish retention time windows for GC methods. Other approaches may be employed, provided that the analyst can demonstrate that they provide performance appropriate for the intended application.

1 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72 hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

2 Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007min). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

4 The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72 hour period or 0.03 minutes, whichever is greater. (If the default standard deviation in Sec. 11.6.3 is employed, the width of the window will be 0.03 minutes.)

5 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

6 The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

7 If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst.

8 The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

Appendix No. 2 - Recommended VOC Sample Preservation Techniques and Holding Times

Sample Matrix	Preservative	Holding Time	Comment
Aqueous Samples With No Residual Chlorine Present	Cool to 4 ± 2°C.	7 days	If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples With No Residual Chlorine Present	Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
Aqueous Samples With Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to 4 ± 2°C.	7 days	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. If MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples. If aromatic and biologically active compounds are analytes of interest, acid preservation is necessary and the holding time is extended to 14 days.
Aqueous Samples With Residual Chlorine Present	Collect sample in a pre-preserved container containing either 25 mg ascorbic acid or 3 mg of sodium thiosulfate per 40-mL of chlorinated sample volume containing less than 5 mg/L of residual chlorine. Cool to 4 ± 2°C and adjust pH to less than 2 with HCl or solid $NaHSO_4$	14 days[1]	Samples containing greater than 5 mg/L of residual chlorine may require additional amounts of dechlorinating agents. Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible. Caution: never add acid preservative directly to a dechlorinating agent prior to sample collection.
Solid Samples[2]	Sample is extruded into an empty sealed vial and frozen on-site to < -7°C.	14 days[1]	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Appendix 2 - Recommended VOC Sample Preservation Techniques and Holding Times Cont.

Sample Matrix	Preservative	Holding Time[1]	Comment
Solid Samples[2]	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C for no more than 48 hours then frozen to < -7°C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C for no more than 48 hours then preserved with methanol upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not preserved with methanol prior to the expiration of the 48 hour period.
	Sample is extruded into an empty sealed vial and cooled to 4 ± 2°C.	48 hours	
	Cool to 4 ± 2°C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Freeze to < -7°C the coring tool used as a transport device	48 hours	The holding time may be extended to 14 days if the sample is extruded to a sealed vial and either frozen to < -7°C or chemically preserved. Coring tools should not be frozen below -20°C due to potential problems with tool seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and frozen on-site to < -7°C.	14 days[1]	Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.
	Sample is extruded into a vial containing reagent water and cooled to 4 ± 2°C for 48 hours or less then frozen to < -7°C upon laboratory receipt.	14 days[1]	Analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48 hour period. Sample vials should not be frozen below -20°C due to potential problems with vial seals and the loss of constituents upon sample thawing.

Appendix 2 - Recommended VOC Sample Preservation Techniques and Holding Times Cont.

Sample Matrix	Preservative	Holding Time[1]	Comment
Solid Samples[2]	Sample is extruded into a vial containing reagent water and 1 g $NaHSO_4$ and cooled to 4 ± 2°C.	14 days[1]	Reactive compounds such as 2-chloroethylvinyl ether readily break down under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.
	Sample is extruded into a vial containing methanol and cooled to 4 ± 2°C.	14 days[1]	Additional methanol extract storage time beyond 14 days may be acceptable if the desired VOC constituent stability can be demonstrated from appropriate performance data.

[1] A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

[2] For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours of sample collection.

WORK INSTRUCTION FOR

Diesel Range Organics (DRO)

Methods: EPA 8015B

Project Specific Requirement for Sparrow Point Project

SOP NUMBER:	WI-PGH-O-002-0
REVIEW:	Danette Cavalier
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	Created from PGH-O-004-7
REVIEW DATE:	Upon Procedural Change

APPROVALS

Kent A Blaul
General Manager — 08/14/15 Date

Maureen K. Rakiewicz
Senior Quality Manager — 08/14/15 Date

Danette Cavalier
Department Manager/Supervisor — 08/14/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1. This SOP documents the procedure to be followed for the analysis of Diesel Range Organics (DRO) by EPA Methods 8015B.

2. Scope and Application

2.1. This SOP may be used to measure the concentration of diesel range organics (defined as C10-C28) and various other hydrocarbon ranges eluting between C10 and C40 (examples: C10-C20, C20-C34, C28-C40) in water, soil and waste.

2.2. State specific Total Petroleum Hydrocarbon (TPH) methods must be followed when they are required.

2.3. This procedure is restricted to use by, or under the supervision of analysts experienced in the operation of a gas chromatograph equipped with flame ionization detector (GC/FID), gas chromatography and the interpretation of gas chromatographic (GC) data. Table 1 contains typical compounds that may be determined by this method.

3. Summary of Method

3.1. This procedure provides gas chromatographic conditions for the measurement and quantitation of semivolatile petroleum fractions such as diesel (fuel oil #2), or kerosene (fuel oil #1). See Table 1 for reporting limits in water and soil.

3.2. Samples are extracted with an organic solvent to remove the constituents of interest. Samples are prepared according to SOP PGH-O-022, Microwave Extraction for solid samples and PGH-O-028, Separatory Funnel Extraction for aqueous samples. The extracts are dried and concentrated and then introduced into the GC/FID system via autosampler.

3.3. Results of the analysis are then processed, reviewed and reported.

4. Interferences

4.1. Major sources of contamination include solvent impurities, impurities in the helium carrier gas, and the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) sealants, tubing, or flow controllers with rubber components is avoided, since such materials out-gas organic compounds. Analyses of reagent blanks provide information about the presence of contaminants.

4.2. Samples may be contaminated by dirty glassware and/or contaminated solvents during extraction. A Method Blank (MB) prepared using organic-free reagent water or baked Ottawa Sand and carried through the entire extraction, handling and storage procedures must be analyzed as part of the sample batch to determine contamination sources that may be outside the chromatographic system. All glassware used to prepare sample extracts should be washed with hot, soapy water and rinsed with water, acetone and methylene chloride to reduce the risk of contamination.

4.3. Contamination may also occur when a sample containing low concentrations of semivolatile organic carbon compounds (SVOC) is analyzed immediately after a sample containing high concentrations of SVOCs. This is referred to as “carryover”. A technique to prevent this is to analyze solvent blanks between sample analyses. After the analysis of a sample containing high concentrations of SVOCs, one or more solvent blanks should be analyzed to check for carryover. If the sample analyzed immediately following the high concentration sample does not contain compounds present in the high level sample, freedom from contamination may be established.

4.4. Heavier and lighter petroleum products may contain some semivolatile components that produce a response within the DRO retention time range. Other compounds that respond to FID (chlorinated and oxygenated hydrocarbons) will be included in the

concentration. If the chromatogram exhibits the characteristics of gasoline, DRO results should be reported and flagged with a recommendation for GRO analysis.

5. Safety

5.1. Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2. The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3. Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1. Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2. Diesel Range Organics (DRO): All resolved and unresolved material eluting from n-decane (n-C10) through n-octacosane (n-C28), inclusive.

6.3. DRO Marker Solution (DMS): A ten or more component blend of diesel compounds (Table 1). This standard defines the retention time window for diesel range organics.

6.4. Diesel Fuel #2 Composite Standard: A commercial blend of Diesel Fuel #2 composite. This standard serves as a calibration standard.

6.5. Surrogate Control Sample: A reagent water or soil blank spiked with the surrogate and taken through the entire procedure with samples, including extraction. This sample may also be referred to as a Method Blank.

6.6. Minimum Reporting Level (MRL): The laboratory reporting level for a commercial diesel fuel oil mixture. The MRL must be greater than or equal to the MDL.

6.7. Column Bleed Blank (CBB): An aliquot of methylene chloride analyzed to determine the contribution to DRO area due to temperature programming baseline elevation (bleed). Results from these blanks may be subtracted from the results of samples if column bleed contributes significantly to the total area.

7. Responsibilities and Distribution

7.1. General Manager/Assistant General Manager (GM/AGM)

7.1.1. The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2. The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2. Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1. The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2. The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3. The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3. Department Manager/Supervisor

7.3.1. The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2. The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3. The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4. The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4. Individual Staff

7.4.1. Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2. Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3. Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1. Aqueous and solid samples are cooled to 4 ± 2°C.

8.2. Water samples must be extracted within 7 days of collection.

8.3. Soil samples must be extracted within 14 days of collection.

8.4. Sample extracts are stored at 4 ± 2°C and must be analyzed within 40 days of extraction.

9. Equipment and Supplies

9.1. Gas Chromatograph: Hewlett Packard Model 5890, or equivalent, equipped with a flame ionization detector (FID), autosampler tray, and autosampler tower.

9.2. Capillary Column: RESTEK Rtx-5 or RTX-5MS, 30m, 0.32 mm ID column, or equivalent.

9.2.1. Capillary Column: Agilent/J&W DB-5, 10 m, 0.32 mm ID, or equivalent.

9.3. Optional Column: RESTEK Rtx-1 30m, 0.53 mm ID column, or equivalent.

9.4. Sample containers: 2mL autosampler vials with PTFE septa lined crimp caps.

9.5. Data System: Chemstation®/Target software. Used for operation of the GC system, acquisition of data and processing of GC information.

9.6. Syringes: Hamilton 10, 25, 50, 100, 250, 500 and 1000µL syringes.

9.7. Glass Pipettes: 1.0mL and 10.0mL, disposable.

9.8. Volumetric Flasks: 10mL, 25mL, Class A, glass.

9.9. Vial cap crimper.

10. Reagents and Standards

(See the Certificates of Analysis and/or the GC Standard Preparation Logbook for the specific recipes to make up the standards listed in this SOP.)

10.1. Methylene chloride: Fisher Brand pesticide grade, or equivalent.

10.2. Organic-free reagent (DI) water: Millipore Super Q®, or equivalent.

10.3. 50000µg/mL Diesel Fuel #2 Composite (DFC) Standard: Restek brand, or equivalent.

10.4. 50000µg/mL Diesel Fuel #2 Composite Standard: Ultra Scientific brand, or equivalent.

10.5. 10000µg/mL ortho-terphenyl (o-tp) Surrogate Stock Standard: Restek brand, or equivalent.

10.6. 2000µg/mL Diesel Range Organics Component Standard: Restek brand, or equivalent.

10.7. 50000µg/mL Diesel/Motor Oil Mixture Standard: Ultra Scientific brand, or equivalent.

10.8. 50000ug/ml Motor Oil Composite Standard: Restek brand, or equivalent.

10.9. Working calibration curve standards are prepared by diluting specific amounts of the above stock standards in methylene chloride. All calibration standards are stored in the standard refrigerator at 4 ± 2°C. Working standards must be replaced after six months, sooner if comparison with check standards indicates a problem or stock standards used to make the working standard expire.

11. Calibration

11.1. The Diesel/Motor Oil Mixture Standard is analyzed at seven concentration levels with the low standard at 100µg/mL and the remaining standards covering the linear range of the detector. The six remaining standards are at concentrations of 200, 300, 400, 500, 1000 and 2000µg/mL.

11.2. The reporting limits based upon the low standard concentration and considering the extraction procedure are 0.10mg/L for aqueous samples and 6.67mg/Kg for solid samples

11.3. The total peak area for the material eluting within the target hydrocarbon range are tabulated against the concentration of the standard injected for each of the calibration levels analyzed. The results are used to prepare a calibration curve by linear regression or to calculate an average calibration factor. The calibration factor (CF) and/or the regression is calculated for each calibration standard by the system software.

11.3.1. When linear regression analysis is used, the correlation coefficient (r) must be 0.99 or greater.

11.3.2. When average CF is used, the relative standard deviation must not exceed 20%.

11.3.3. For 2nd order curves such as quadratic the coefficient of determination (COD) must be (r2 ≥ 0.99 or better). Second order curves should only be used in circumstances where a linear curve is clearly not appropriate. While quadratic curves are generally reliable within the calibration range, they can produce highly erroneous results above the calibration range, including negative numbers at high concentrations.

11.4. Retention time windows are used to identify the target range in sample and standard chromatograms. Analyst experience should weigh heavily in the use of retention time windows and the identification of target ranges. See the procedure described in Appendix No. 1 of this SOP for the determination and setting of retention time windows.

11.4.1. The retention time range is established from the retention times of the first and last alkane of the target hydrocarbon range (i.e., for DRO C10 and C28). The retention time range is then calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

11.5. Each time a new calibration curve is established, the curve must be verified with a standard from a second source (ICV). The initial calibration verification standard (ICV from second source) must be within ±20% of the initial calibration response.

11.6. The working calibration curve must be verified on each working day, and after every 20 samples, by the injection of a calibration standard. Each continuing calibration standards (CCV) must be within ±15% of the initial calibration response for 8015B.

11.7. Removal of Points from a Calibration Curve:

11.7.1. Removing or replacing of points from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. The curve is evaluated with the levels removed. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve must be reanalyzed. Corrective action may include instrument maintenance and/or repreparation of standards. If the low standard is dropped, then the lowest remaining calibration point must be at or below the reporting limit.

11.8. Basic Elements of Calibration Review:

11.8.1. The lowest calibration level must be at or below the RL. If this requirement is not met, the instrument must be recalibrated to include a lower concentration standard. The lowest calibration level must be higher than the MDL.

11.8.2. The minimum number of calibration points requirement must be met. If not, the instrument must be recalibrated.

11.8.3. Linearity requirements as stated in this SOP must be met. If this requirement is not met, the problem must be investigated, fixed, and the instrument recalibrated.

11.8.4. Examine the plots for Quadratic fits: The calibration plots must be visually examined to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal.

11.8.5. The y-intercept should be < ½ RL when reporting to the RL and < MDL when reporting to the MDL.

11.8.6. Increasing Response with Increasing Concentration: The instrument signal should increase with every increase in standard concentration.

12. Procedure

12.1. Samples and standards are removed from their respective refrigerators and allowed to warm for a minimum of thirty minutes.

12.2. Hydrogen and compressed air to the FID are turned on and the flame is ignited.

12.3. Prepare the appropriate standards (either an initial calibration or continuing calibration verification) by labeling an autosampler vial(s) with the appropriate standard ID(s) and placing micro inserts into the vials. Transfer an aliquot of standard to the appropriate vial(s). Cap the vial(s) with a PTFE lined crimp cap and crimp it closed.

12.4. Prepare samples for analysis in the same manner as the standards, labeling the autosampler vials with the appropriate sample ID(s).

12.5. Prepare several methylene chloride blanks by transferring an aliquot of methylene chloride to 2mL autosampler vials.

12.6. Place all appropriate blanks, standards, QC sample and client sample extracts in the 2mL autosampler vials on the autosampler tray as follows:

- Methylene chloride blank (at least one, more may be required).
- DRO Marker Solution (DMS),
- Calibration standard (either ICAL or CCV),
- ICV (only if initial calibration is analyzed),
- DRO Marker Solution (DMS),
- Methylene chloride blank (CBB),
- Samples to be analyzed (up to 20, including the Method Blank and LCS/LCSD).
- CCV standard.
- Methylene chloride blank.

(Analysis may continue beyond this point depending upon the number of samples to be analyzed and calibration verification results).

12.7. Set up the sequence to be analyzed in the Agilent Technologies ChemStation® software.

12.8. Sample injections may continue for as long as the calibration verification standards meet QC requirements. Standards are analyzed after every 20 extracted samples. The sample injection sequence ends when all samples and bracket verification standards have finished, or at the point of the last acceptable verification standard.

12.9. Following analysis, the raw data files are processed using the Target® chromatography software. Processing includes integration of chromatographic peaks and identification of analytes according to parameters set up in the particular processing method.

12.10. Integration for TPH in samples is performed on a baseline-to-baseline basis as opposed to a valley-to-valley integration. The resulting chromatogram from the CBB may be subtracted from sample and standard chromatograms to correct for area generated by the rise in baseline due to column bleed, if necessary.

12.11. Any sample with a result that exceeds the initial calibration range, must be diluted and re-analyzed.

12.12. All client samples, blanks, and QC samples must be evaluated according to the criteria listed in Section 14. Any exceptions must be evaluated by the analyst and the Group Leader and documented in the final report.

12.13. Once the samples have been analyzed, a report is generated by the Target® software or equivalent. This report shows the RT, the expected RT, the response, the on-column concentration, the final concentration, and the surrogate recovery report.

12.14. Each instrument has a run logbook in which all analyses performed including blanks, standards, client samples and QC samples are recorded. Other information documented includes analyst initials, date of analysis, sample identification, dilution factor, injection volume, and instrument and raw data file identifications. A new folder containing standard and QC data is created each day and dated.

12.15. Daily Analytical Batch Files

12.15.1. Copies of the ICAL, CCAL, extraction logs, and batch sheets are maintained in folders according to the instrument identification and date of analysis.

12.15.2. Raw data files are maintained on the computer data system and are backed up as necessary.

13. Calculations

13.1. Water Samples:

$$Concentration(mg/Kg) = \frac{(Ax)(Df)(V)}{(RF)(Vo)}$$

Where:
Ax = Area of compound to be measured
RF = Response factor from the ICAL, for a specific compound
Df = Dilution factor
V = Final volume of sample extract in milliliters (mL)
V_o = Volume of water extracted in milliliters (mL)

13.2. Soil Samples:

$$Concentration(mg/Kg) = \frac{(AX)(Vt)(Df)}{(RF)(Ws)(D)}$$

Where:
Ax = Area of the compound to be measured
RF = Response factor from the ICAL, for a specific compound
Ws = Weight of sample extracted in grams (g)
D = (100-%moisture)/100
Vt = Final volume of sample extract in milliliters (mL)

13.3. Calibration Factor

$$CF = \frac{A_s}{C_s}$$

Where:

A_s = Peak area of the analyte or surrogate
C_s = Concentration of the analyte or surrogate.

13.4. Average Calibration Factor:

$$CF_{avg} = \frac{\sum(individualCFs)}{number\_of\_standards}$$

13.5. Using the calibration standards, the system software will calculate the percent relative standard deviation (%RSD) for each compound using the following equation:

$$\%RSD = \frac{(SD_{CF})}{CF_{avg}} x100$$

Where:
SD_{CF} = the standard deviation for the CFs of each compound
CF_{avg} = the average of the CFs for each compound

13.6. Matrix Spike/ Duplicate, and/or LCS/LCSD

$$\%\,Recovery = \frac{C_{ss} - C_s}{S} x100$$

Where:

Cs = Concentration of the source sample
Css= Concentration of the spiked sample
S = Amount spiked

$$RPD = \frac{\left|(R_{MS} - R_{MSD})\right|}{(R_{MS} + R_{MSD})/2} x100$$

Where:

R_{MS} = Matrix Spike recovery
R_{MSD} = Matrix Spike Duplicate recovery

14. Quality Control

14.1. A method blank, LCS, and MS/MSD must be prepared with each analytical batch, not to exceed twenty samples. If insufficient sample is provided for MS/MSD, it shall be noted in the project final report.

14.1.1. The method blank may not contain the target hydrocarbon ranges above the RL. If the blank contains a positive that is above the RL, the samples associated with that blank should be re-extracted and reanalyzed if possible. If re-extraction and reanalysis is not possible, results for the affected samples must be flagged and the problem noted in the project final report.

14.1.1.1. Client specific requirements may require method blanks to be evaluated to less than ½ the RL.

14.1.2. Percent recoveries for the LCS must be within the laboratory established generated limits listed in Table 3.

14.1.3. Matrix Spike and Spike Duplicate (MS/MSD) samples are analyzed in the same manner as all other samples. If recovery is not within the laboratory established limits listed in Table 3, but the LCS is within the acceptable range, matrix interference is assumed.

14.2. Acceptance criteria for surrogate recovery are listed in Table 4. If the surrogate recoveries are not within the limits, perform the following procedures:

14.2.1. Check the standard to ensure that it has been properly prepared and that it has not been concentrated. If problems are found, prepare a new surrogate standard and reextract and reanalyze the samples.

14.2.2. Check for errors in the calculations. If an error is found, recalculate the data accordingly.

14.2.3. Check instrument performance. If a problem is identified, such as standard degradation, correct the problem and reanalyze the sample(s).

14.2.4. Some samples may contain peaks that interfere with the elution of the surrogate standard (matrix interference). In samples containing TPH, the surrogate peak may need to be manually integrated to achieve an accurate peak area.

14.2.5. If surrogates are outside the acceptance limits, reanalysis of the affected samples is required.

14.2.5.1. If upon reanalysis the recoveries are outside the limits, report the results of the original analysis and document the matrix interference in the project final report.

14.2.5.2. If the recoveries of the reanalysis are within the limits and the sample was reanalyzed within the recommended holding time, report the results of the second analysis and document this in the project final report. If the holding time has expired prior to reanalysis, consult with the supervisor and/or the quality department to determine which results are to be reported. If results must be used for the analysis performed outside of the holding time, notify the appropriate Project Manager and document this in the project final report. Exception: If the surrogate recoveries in the sample used for MS/MSD analysis were outside the acceptance limits, then it should only be reanalyzed if the recoveries met the acceptance criteria in both the MS and MSD.

14.3. A CCV(s) is analyzed at the beginning and end of each analytical sequence. The CCV(s) must be run after every twenty sample injections or every 12 working hours, whichever is more frequent. The CCV RFs must be within 15% of the initial calibration RFs for 8015B.

14.4. Corrective Actions for Out-Of-Control Data

14.4.1. Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.4.2. Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.4.2.1. The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.4.3. Matrix Spike Recovery (MS) – If the Matrix Spike recoveries do not meet the acceptance criteria, the batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the spike recovery is not within the 25% RPD, a note is included in LIMS.

14.4.4. An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.4.5. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report

15. Method Performance

15.1. As indicated, the use of this method is restricted to use analysts experienced in the operation of a GC system.

15.2. The instrument must meet all the criteria for calibration and standardization

15.3. Method performance is achieved through the analysis of MDLs, demonstration of capability (DOC) tests (annual) and/or Performance Evaluation samples and in-house laboratory Quality Control samples.

15.4. MDL standards are to be made up with a Diesel/Motor Oil Mixture Standard.

15.5. Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.6. An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.7. On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1. All sample preparation involving the use of organic solvents (methylene chloride, for example) is performed in a fume hood.

16.2. Sample solvent extracts and solvent rinses are collected in appropriately labeled containers and disposed of in the designated waste streams.

17. References

17.1. USEPA, SW-846 III Ed., Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Methods 8015B, Revision 2, December 1996.

17.2. Total petroleum hydrocarbons (TPH) as Gasoline and Diesel, SW-846 Method 8015B (Revision 2, December 1996) EPA Addendum Tables.

17.3. USEPA, SW-846, Third Ed., Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

17.4. USEPA, SW-846, Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

17.5. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.6. TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.7. Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.8. SOP PGH-C-030, Manual Integrations, current version.

17.9. SOP PGH-C-032, Support Equipment, current version.

17.10. SOP PGH-C-035, MDL-LOD, current version.

17.11. SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.12. SOP PGH-Q-038, Laboratory Equipment, current version.

17.13. SOP S-ALL-Q-011, Audits, current version.

17.14. SOP S-ALL-Q-012, Corrective Action, current version.

17.15. SOP S-ALL-Q-020, Training, current version.

17.16. SOP S-ALL-Q-028, Lab Track, current version.

17.17. SOP PGH-C-027, DI Water, current version.

17.18. SOPs PGH-O-028 Separatory Funnel Extraction, current version.

17.19. SOP PGH-O-022 Microwave Extraction, current version

17.20. SOP PGH-O-011, Waste Dilution Extraction, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1. Table 1: Typical Hydrocarbon Ranges and Reporting Limits.

18.2. Table 2: Guidelines for GC operating conditions.

18.3. Table 3: DRO Control Limits LCS/MS/MSD

18.4. Table 4: DRO Surrogate Control Limits

18.5. Appendix 1: Determination of Retention Time Windows.

19. Equipment Maintenance

19.1. In order to keep the instrument running at peak performance, it will be necessary from time to time to perform some type of maintenance on the instrument. All maintenance performed on a particular instrument will be documented in the Instrument Maintenance Logbook for that instrument. This documentation will include not only the actual maintenance performed, but also the reason the maintenance is deemed necessary and the results of the maintenance.

19.2. Injection port

19.2.1. Many issues with chromatographic performance can be attributed to a dirty or contaminated injection port. A misplaced column (i.e., too much or too little column projecting past the column nut ferrule) can also cause poor performance. Symptoms of injection port issues include, but are not limited to, degradation of analytes, small, broad peaks, peak tailing, peak fronting, noisy baseline, ghost peaks, and retention time shifts.

19.2.2. The issues of degradation, noisy baseline, or ghost peaks can usually be resolved by replacing the glass wool in the injection port liner. If there is no wool in the liner or replacement of the wool fails to resolve the issue, the liner itself should be replaced. In most cases this will resolve the issue. If the issue persists, the injection port itself should be cleaned with solvent.

19.2.3. Peak tailing and fronting are typically a result of poor column placement in the injection port. The tip of the column should extend 3 to 5 mm beyond the tip of the ferrule in the column nut. When tailing or fronting occurs, the positioning of the column should be checked and modified if needed.

19.2.4. Retention time shifts are generally a result of loose connections or a cored injection port septum. Tightness of column nuts, adapter nuts and septum caps should be checked and tightened as needed. If the septum shows signs of coring, it should be replaced. A cored septum may also result in ghost peaks as unvolatilized solvent can become trapped in the hole left by the core.

19.2.5. The injection port septum should be replaced every time any injection port maintenance is performed.

19.3. Detectors

19.3.1. Through continued use, the FIDs that are employed in this procedure can become dirty and/or contaminated, build up ash, or corrode, resulting in high baselines, noisy baselines and non- linear response.

19.3.2. Optimal operating signals strength for the FIDs used in this procedure are <30. Response may be acceptable above this value, but as they continue to rise, performance will deteriorate.

19.3.3. When results from the FIDs become erratic, the detectors should be removed from the instrument, disassembled and cleaned.

19.4. Columns

19.4.1. Through continued use, contaminants can deposit on the front end of the column, causing erratic performance including noisy baseline, small broad peaks, and poor resolution.

19.4.2. To resolve these problems, the front end of the column should be clipped by removing 2 to 5 inches.

19.4.3. Eventually, the gains in performance achieved from clipping the column will be outweighed by the loss of resolution due to the shorter column. At this point, the column should be replaced.

19.4.4. After prolonged use, due to the continual heating and cooling of the column, the column will begin to lose stationary phase, resulting in poor resolution and increased column bleed. When resolution or column bleed becomes unacceptable, the column should be replaced.

20. Method Modifications

20.1. Background subtractions for column bleed are performed electronically via the data system rather than numerically as indicated in the method.

20.2. The laboratory uses Method 8015B for diesel range organics (DROs) and other classes of analytes, fuel types and petroleum hydrocarbons other than DROs.

21. Revisions

Document Number	Reason for Change	Date
WI-PGH-O-002-0	1. Created project specific work instruction using the PGH-O-004 for the Sparrows Point project to add the requirements of Table 3 from 8015B Addendum Rev.2 Dec 1996. 2. In this work instruction Table 3 limits for LCS and MS were updated. Table 4 was added for surrogate limits for water and solid matrices.	14Aug2015

Table 1: Typical Hydrocarbon Ranges and Reporting Limits

Hydrocarbon Range	Water (µg/L)	Soil (mg/Kg)
C10-C20	100	6.67
C10-C28	100	6.67
C20-C34	100	6.67
C10-C36	100	6.67
C28-C40	100	6.67

Table 2: Guidelines for GC Operating Conditions

Instrument Operating Conditions

Gas Chromatograph

Carrier Gas	Helium
Initial Temperature	50°C
Initial Hold Time	0.50 minute
Ramp Rate	30°C/minute
Final Temperature	330°C
Final Hold Time	7.17 minute
Injection Port Temp.	250°C
Detector Temp.	300°C

LTM Modules

GC Conditions

Oven Temperature 280°C

Injector Temperature 280°C

Detector Temperature 340°C

Module Program: 55°C for 0.50 min. to 330°C @ 150°C/min. hold for 2.1667 min.

Table 3: DRO Control Limits LCS/MS/MSD

	Water & Solid	Water & Solid	Water & Solid
Parameter	**LCS % Recovery**	**Matrix Spike % Recovery**	**RPD (%)**
Diesel Component	80-120	65-135	30
C10-C20	80-120	65-135	30
C10-C28	80-120	65-135	30
C20-C34	80-120	65-135	30
C28-C40	80-120	65-135	30

Table 4: DRO Surrogate Control Limits

Surrogate	**Water % Recovery**	**Solid % Recovery**
o-Terphenyl	75-125	60-125

Appendix No. 1 - Determination of Retention Time Windows EPA Method 8000C (Section 11.6)

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC and HPLC methods that do *not* employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

The following subsections describe one approach that may be used to establish retention time windows for GC methods. Other approaches may be employed, provided that the analyst can demonstrate that they provide performance appropriate for the intended application.

11.6.1 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72 hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

11.6.2 Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007min). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

11.6.3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

11.6.4 The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period or 0.03 minutes, whichever is greater. (If the default standard deviation in Sec. 11.6.3 is employed, the width of the window will be 0.03 minutes.)

11.6.5 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

11.6.6 The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

11.6.7 If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst.

11.6.8 The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

WORK INSTRUCTION FOR

Analysis of Polychlorinated Biphenyls (Aroclors)
Methods: EPA 8082 & 8082A
Project Specific Requirement for Sparrow Point Project

SOP NUMBER:	WI-PGH-O-038-0
REVIEW:	Danette Cavalier
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	Created from PGH-O-009-10
REVIEW DATE:	Upon Procedural Change

APPROVALS

Kent A Blaul
General Manager — 07/07/15 Date

Maureen K. DeFabio
Senior Quality Manager — 07/07/15 Date

Danette Cavalier
Department Manager/Supervisor — 07/07/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This SOP documents the procedure to be followed for the analysis of polychlorinated biphenyls Aroclors) by EPA Method 8082 and 8082A.

2. Scope and Application

2.1 This procedure is used for the analysis of Aroclors in water, soil, wipes and waste.

2.2 The following Aroclors may be determined by this method:

Aroclor-1016
Aroclor-1221
Aroclor-1232
Aroclor-1242
Aroclor-1248
Aroclor-1254
Aroclor-1260
Aroclor-1262
Aroclor-1268

2.3 This method is restricted to use by, or under supervision of, an analyst trained in the use of gas chromatographs and skilled in the interpretation of gas chromatograms.

2.4 The reporting limits for the individual Aroclors in water are 0.25µg/L when the initial sample volume is 1 liter and the extract final volume is 5 mL. The reporting limits for the individual Aroclors in soil are 0.0167 mg/Kg when the initial sample mass is 15g and the extract final volume is 5 mL.

3. Summary of Method

3.1 Aqueous sample are prepared as per SOP PGH-O-028, Separatory funnel extraction. Solid samples are extracted as per SOP PGH-O-022, Microwave extraction.

3.2 An aliquot of the sample extract (0.5-1uL) is injected into the injection port of the GC where it is vaporized. The sample is then eluted onto the GC column with an inert gas flowing at a predetermined rate. The sample is chromatographically separated into its individual constituents by the column as it passes through the stationary phase and is detected by the Electron Capture Detector (ECD). The change in electronegativity by loss of free electrons from the charged sample molecules is directly related to the quantity of the analyte in the sample. The response is detected by the ECD as a change in electrical current. The concentration of Aroclors is a function of the response of the peaks produced by the change in current.

4. Interferences

4.1 Contaminated solvents, reagents, or sample processing hardware.

4.1.1 Phthalate esters introduced during sample preparation are a major source of contamination and can interfere in Aroclor® determinations. Common flexible plastics contain varying amounts of phthalate esters, which are easily extracted or leached from such materials during laboratory operations. Interference from phthalate esters can be best minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. These materials can be removed through the use of sulfuric acid cleanup.

4.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces, may cause interferences.

4.2.1 GC inlet liners and column should be replaced or cut as sample residue builds up or as calibration/QC results indicate.

4.2.2 GC injectors may need to be cleaned. Refer to the appropriate GC manual for instructions.

4.2.3 ECD detectors may become contaminated or worn after extended use. The detectors are returned to an authorized vendor for cleaning as necessary.

4.2.4 All carrier and make-up gases are ultra-high (99.999%) purity and all are passed through oxygen/water and hydrocarbon filters before introduction to the GC.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc Quality Manual for the definitions used throughout this SOP.

6.2 Aroclor is a registered trademark of Monsanto Corp.

7. Responsibilities and Distribution

7.1. General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Extracts must be stored refrigerated (4±2ºC) and protected from light.

8.2 Sample extracts must be analyzed within 365 days of extraction.

9. Equipment and Supplies

9.1 Gas chromatograph: an analytical system complete with gas chromatograph with injector (1/4 inch), open glass sleeves, HP Green 11mm septa, and autosampler (towers and trays) with 10µL syringes for direct injection on two dissimilar phase analytical columns (DB-17MS and HP-5 or equivalent), dual electron capture detectors (ECDs), and a data system (Agilent Chemstation® software) for data acquisition, and (ThruPut Target® Analytical software) for data reduction.

9.2 Dual Column Set-up:

- Column 1: 20m x 0.18mm ID fused silica DB-17MS, 0.18 µm film thickness, or equivalent.
- Column 2: 20m x 0.18mm ID fused silica HP-5, 0.18 µm film thickness, or equivalent.
- Optional Column 1: 30m X0.53mm ID fused silica RTX-1701, 0.5µm film thickness, or equivalent.
- Optional Column 2: 30 m x 0.53 mm ID fused silica RTX-5 (5% diphenyl 95% dimethyl polysiloxane phase), 0.5µm film thickness, or equivalent.
- Direct Injection Tee (for dual 0.32 and 0.53 mm ID fused silica capillary columns).
- Universal angled Y column connector.

9.3 Gases

- Carrier: ultra-high purity helium: ~2-5 mL/minute exit flow.
- Ultra-high purity nitrogen: ~50 mL/min exit flow.

9.4 External Gas Traps: Oxygen and hydrocarbon traps are installed, in series, on each of the two gas lines.

9.5 Autosampler Vials: 2mL glass 11mm vials with PTFE crimp caps and crimper/decrimper apparatus.

9.6 Other Materials/Supplies:

- Volumetric flasks,10mL, 25mL, and 100mL, Class A, glass.
- Syringes 1000µL, 500µL, 100µL, 50µL, 10µL.
- 4 mL amber and clear vials and open-top screw caps with PTFE septa.
- 20 mL scintillation vials with screw caps.
- 5 ¾ inch disposable Pasteur pipettes.
- 2mL blue pi-pump & 5-10mL green pi-pump, and pipette bulbs.
- Repipetter fitted to 4L solvent bottle.

10. Reagents and Standards

10.1 Solvents

10.1.1 Hexane: Pesticide grade, or equivalent.

10.2 Standards

10.2.1 Calibration curve standards and mid-level verification: prepared using stock standards purchased as certified solutions in hexane from Restek or equivalent (See the department standards logbook for guidance in preparation of standard and clean-up solutions).

10.2.2 Initial Calibration Verification (ICV) standard solutions are prepared from certified stock solutions purchased from Ultra Scientific and/or Restek, or equivalent.

10.3 Reagents Used for Sample Extract Clean-up

10.3.1 Tetrabutylammonium (TBA) Sulfite Solution

10.3.1.1 Tetrabutylammonium hydrogen sulfate

10.3.1.2 Sodium Sulfite

10.3.1.2.1 Prepare reagent by dissolving 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL of organic-free reagent water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts (top layer) and add 25 g of sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a PTFE-lined screw cap. This solution is stored at room temperature and is replaced when no longer effective for extract cleanup.

10.3.2 Sulfuric Acid (Concentrated, 18N).

10.3.3 Organic-free reagent DI water (ASTM Class II or equivalent: Milli-Q)

11. Calibration (applies to both primary and confirmation columns)

11.1 Initial Calibration: External standard calibration is used for Aroclor analysis.

11.1.1 Calibration is achieved through the analysis of standards containing the target analytes at a minimum of five different concentrations covering the working range of the instrument.

11.1.1.1 Six concentrations of Aroclors 1016 and 1260 (AR1660) and surrogates are used for the initial calibration.

11.1.1.2 Concentrations of AR1660 and surrogates in the ICAL are 0.05, 0.10, 0.25, 0.50, 0.75 and 1.0 mg/L.

11.1.1.3 Single point standards for identification and quantitation purposes are analyzed for the remaining Aroclors at 0.25 mg/L.

11.1.2 Calibration standards are introduced into the chromatographic system in the same manner used to introduce actual samples (i.e. 1 µL injection via programmable autosampler into a heated injection port).

11.1.3 A minimum of five peaks for each, Aroclor shall be used for calibration. The exception is Aroclor 1221 where three peaks will be used.

11.1.4 Calibration factors (CFs) are determined for each of the five peaks chosen for quantitation for each particular Aroclor, in each calibration standard analyzed, including surrogates. The response factor for each Aroclor at each concentration equals the Aroclor peaks' response in the standard divided by the concentration of that Aroclor in the standard (i.e. CF = Response of particular Aroclor in standard/concentration of Aroclor in standard).

11.1.5 Response of analytes is measured as peak area, remaining consistent through the life of the calibration. When peak area is chosen for a particular analyte, it MUST be used for that analyte in all initial calibration standards and all subsequent calibration verification standards and samples which are associated with that initial calibration.

11.1.6 Linearity of the initial calibration is determined through the use of the average CF and relative standard deviation (RSD). For each analyte and surrogate analyzed, calculate the average CF, the standard deviation (SD), and the RSD as follows:

$$Average\ CF = CF_{AVG} = \Sigma CF_i / n,$$

$$SD = \sqrt{(\Sigma (CF_i - CF_{AVG})^2 / n-1)}, \text{ and}$$

$$RSD = (SD / CF_{AVG}) \times 100,$$

Where:

n = the number of calibration standards and
CF_i = the CF of each individual standard.

11.1.7 If the RSD of the calibration factors for a given Aroclor or surrogate is less than or equal to 20% over the calibration range, then linearity is assumed, and the average CF may be used to determine sample concentrations for that analyte.

11.1.7.1 The RSD for each of the five peaks chosen for a particular Aroclor shall be less than or equal to 20%.

11.1.7.1.1 For Method 8082: If one or more of the RSDs exceeds 20%, the calibration may still be acceptable provided that the average of the five RSDs for that particular Aroclor is less than or equal to 20%.

11.1.7.1.2 For Method 8082A: The RSD for each of the five peaks chosen for a particular Aroclor shall be less than or equal to 20%.

11.1.8 If the RSD for a particular Aroclor or surrogate exceeds 20%, then corrective action must be taken before any sample analysis may begin if that analyte is to be determined using this procedure.

11.1.9 Alternatively, the initial calibration curve may be evaluated using linear regression provided the correlation coefficient (r) is greater than or equal to 0.99.

11.1.9.1 If the RSD is greater than 20% and if the correlation coefficient falls below the acceptance limit, linear regression cannot be used and a second-order regression (quadratic) could be attempted.

11.1.10 Non-Linear Calibration

11.1.10.1 When the instrument response does not follow a linear model over a sufficiently wide working range, or when the previously described calibration approaches fail acceptance criteria, a non-linear, second-order calibration model may be employed. The second-order calibration uses the following equation:

$$y = ax^2 + bx + c$$

Where a, b, and c are coefficients determined using a statistical regression technique; y is the instrument response; and x is the concentration of the target analyte in the calibration standard.

A minimum of six points must be used for a second-order regression fit.

11.1.10.2 The coefficient of determination must be $r^2 \geq 0.99$. Second-order regressions should be the last option.

11.1.10.3 Before selecting a second-order regression calibration model, it is important to ensure the following:

- The absolute value of the intercept is not large relative to the lowest concentrations being reported.
- The response increases significantly with increasing standard concentration (i.e., the instrument response does not plateau at high concentrations).
- The distribution of concentrations is adequate to characterize the curvature.

11.1.11 If all fails, perform appropriate corrective actions necessary and analyze a new calibration curve.

11.2 The same calibration model used for the initial calibration must be used for all subsequent analyses of standards and reagents until the next initial calibration. The model utilized can not be changed after the ICAL has been processed and approved.

11.3 **Removal of Points from a Calibration Curve:**

11.3.1 Removing or replacing of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. The curve is evaluated with the levels removed. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve must be reanalyzed. Corrective action may include instrument maintenance and/or repreparation of standards. If the low standard is dropped, then

the lowest remaining calibration point must be at or below the reporting limit.

11.4 **Basic Elements of Calibration Review**:

11.4.1 The lowest calibration level must be at or below the RL. If this requirement is not met the instrument must be recalibrated to include a lower concentration standard. The lowest calibration level must be higher than the MDL.

11.4.2 The minimum number of calibration points requirement must be met. . A minimum of five calibration standards is required. For 2nd order quadratic curve a minimum of 6 calibration standards is required. If not the instrument must be recalibrated.

11.4.3 Linearity requirements as stated in this SOP must be met. If this requirement is not met, the problem must be investigated, fixed and the instrument recalibrated.

11.4.4 Examine the plots for quadratic fits: The calibration plots must be visually examined to ensure that the fitted function does not re-curve, producing multiple concentrations for a single instrument signal.

11.4.5 Y-intercept: should be < ½ RL when reporting to the RL and <MDL when reporting to the MDL.

11.4.6 Increasing Response with Increasing Concentration: The instrument signal should increase with every increase in standard concentration

11.5 The initial calibration is verified by the analysis of an Initial Calibration Verification (ICV) standard made from a source different than that used for the initial calibration standards. The ICV is analyzed for each Aroclor® (0.25mg/L for all Aroclors) and surrogates. The recoveries of the ICV must be within 80-120%.

11.6 Calibration Verification (applies to both primary and confirmation columns)

11.6.1 To insure that the calibration relationship established during initial calibration is still valid, calibration verification standards must be analyzed at periodic intervals throughout the analysis of mid-level concentration standards. Concentrations other than the mid-level may be used, but the mid-level concentration is typically employed. The AR1660 standard (1016 and 1260 mix), including surrogates, at a concentration of 0.25 mg/L is analyzed as the calibration verification standard because the peaks present in this mixture encompass the entire range of peaks that are present in each of the other Aroclors.

11.6.2 Calibration verification standards are analyzed under the same conditions as any other standards and/or samples analyzed by this procedure.

11.6.3 A calibration factor is determined for each analyte and surrogate in the CVS. The percent difference (%D), is calculated as follows:

$$\% \text{ Difference} = \%D = ([\text{Average CF}] - [CF_{CVS}])/[\text{Average CF}] * 100,$$

Where:

[Average CF] = The average calibration factor calculated for the initial calibration
$[CF_{CVS}]$ = The calibration factor for the continuing verification standard

11.6.4 If the %D for each analyte and surrogate is less than or equal to ±15% for Method 8082 and ± 20% for Method 8082A, then the initial calibration

is considered valid, and the CFs from the initial calibration may still be used to quantitate sample results and analysis may continue.

11.6.4.1 For Method 8082: Should any analytes fail the %D criteria, the initial calibration as a whole for a given Aroclor may still be considered valid if the %D between the average CF for each of the five peaks chosen for the quantitation of a given Aroclor and the average of the five CFs for that Aroclor from the calibration verification does not exceed ±15%.

11.6.4.2 For Method 8082A: Should any analytes fail the %D criteria (± 20%), the initial calibration would no longer be valid for that given Aroclor.

11.6.5 Should none of the situations in 11.6.4 apply, then corrective action is required before analysis can continue.

11.6.6 Calibration verification shall be performed at the beginning of each 12 hour period or after injection of each batch of 20 samples, whichever is more frequent. The time between injection of calibration verification standards shall not exceed 12 hours regardless of whether twenty samples have been injected or not. If there are not sufficient sample extracts to analyze a batch of up to 20, calibration verification should be performed after the analysis of the last sample in the analytical sequence.

11.7 Retention time windows are used to identify the target analytes in sample and standard chromatograms. Analyst experience should weigh heavily in the use of retention time windows and the identification of target analytes. See the procedure described in Appendix No. 1 of this SOP for the determination and setting of retention time windows.

11.7.1 A DDT analog standard should be analyzed each time new retention time windows are determined to ensure that common single component pesticides such as DDT, DDD and DDE do not co-elute with any Aroclor peaks to be used for quantitation.

12. Procedure

12.1 Chromatographic conditions – Prior to analysis, the gas chromatographic system should be operating reliably and the system conditions optimized for the targets that are to be analyzed. For Aroclor analysis, the GC operating conditions are as follows:

12.1.1 GC Instrument Conditions are as follows:(RTX-1701/RTX-5 pair)

Oven: 185ºC for 1 minute to 270ºC @ 7ºC/min, hold 5.25 min.

Injectors: 210ºC

ECDs: 325ºC

Injection volume: 0.5-1 µL

Autosampler syringe rinses/pulses: 5 each

Carrier gas = Ultra high purity helium at ~ 2.0-5.0 mL/min

Make-up gas = Ultra high purity nitrogen at ~ 50 mL/min

Autosampler settings

Syringe capacity = 10 µL

Injection speed = normal

Viscosity delay = 3

Injection volume = 1.0 µL

Pre-injection sample washes = 3

Sample pumps = 3

Post-injection Solvent washes = 5

12.1.2 Instrument Conditions for MACH Unit(DB-17MS and HP-5)

GC Conditions

Oven Temperature = 280^{o}C

Injector Temperature = 210^{o}C

Detector Temperature = 250^{o}C (both)

Carrier Flow = 21.6 mL/min (both)

Makeup = 20 mL/min (both)

DB-17MS and HP-5 Temperature program: 120^{o}C to 220^{o}C at 100^{o}/min. hold one min. to 305^{o}C at 50^{o}/min to 330^{o}C at 300^{o}/min hold 2.05 min.

12.1.3 Autosampler syringe solvent rinse vials should be filled with fresh, clean hexane prior to the beginning of analysis. The waste vials should also be emptied.

12.2 Preparation of standards and sample extracts for analysis: Standards and samples need to be placed in vials and labeled prior to introduction to the chromatographic system.

12.2.1 Remove standards and sample extracts from their respective storage refrigerators. Allow the standards and extracts to warm to room temperature for at least 15 minutes.

12.2.2 As the solutions are warming, label 2.0 mL autosampler vials for each standard and sample to be analyzed. Standards should be labeled with standard ID. Label samples with the particular sample ID and any dilution factor.

12.2.3 Use 300 or 500µL inserts for all standards and any sample which will be analyzed undiluted to save standard and extract volume and minimize waste.

12.2.4 When the standards and sample extracts have warmed sufficiently, transfer an appropriate volume to the corresponding labeled autosampler vial using a disposable Pasteur pipette. Seal the vial with an 11 mm crimp top cap with PTFE lined septa using the crimping tool.

12.2.5 Dilutions

12.2.5.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover. It may also

be necessary to dilute samples because of matrix interferences

12.2.5.2 Dilutions Due to Matrix Interference: If the sample is initially analyzed at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately one half the response of the mid-level calibration standard.

12.2.5.3 Sample surrogate recoveries are considered diluted out above a 20X dilution.

12.2.6 Once all the necessary standard and sample vials have been prepared, data acquisition may begin.

12.3 Data acquisition: Preparation of analysis sequence and introduction of samples to the chromatographic system for collection of raw data.

12.3.1 Load standard and sample vials on to the autosampler tray in the appropriate order. The typical analytical sequence is as follows:

12.3.1.1 It is optional to run one or more primer solutions to desensitize the system. This primer may be a sample, spiked sample, LCS or a standard that is up to the concentration of the highest standard. One or more hexane blanks to demonstrate instrument cleanliness.

12.3.1.2 Applicable calibration standards, either initial or verification, as appropriate.

12.3.1.2.1 Sample analysis may proceed provided that the calibration criteria are met.

12.3.1.3 Up to 20 unknown sample extracts including method blanks, field samples and QC samples. Hexane blanks, if any, injected between samples and standards, to prevent carry-over are not counted as part of the 20.

Calibration verification standards: Sections 12.3.1.2 through 12.3.1.3 may be repeated until such time as:

- All samples in the set have been analyzed.
- A calibration verification standard fails to meet the criteria. In this case, reanalyze samples injected after the last acceptable calibration verification standard (i.e., samples must be bracketed by acceptable calibration verification except as in Sections 12.3.1.4 and 12.3.1.6).

12.3.1.4 If the continuing calibration on one or both columns is outside of this acceptance window showing increased response for particular compounds and these compounds are not present in the sample, the results may be considered valid.

12.3.1.5 If the continuing calibration on both columns is outside of this acceptance window showing decreased response for particular compounds or increased response and the presence of these compounds in the sample, the analysis

must stop and corrective action taken according to Sections 15.8.1 of this SOP.

12.3.1.6 If the continuing calibration is acceptable on one column but is outside the acceptance window on the confirmatory column, results may be reported from the column with the acceptable calibration standard. A project narrative will be added to the final report indicating the failure of the confirmatory column's calibration standard.

12.3.1.7 The analytical sequence must end with the injection of a calibration verification standard, regardless of whether the number of sample injections since the last acceptable calibration verification standard is less than twenty.

12.3.1.8 An acquisition sequence is prepared using the Agilent Chemstation® software. Refer to the specific software User's Guide and/or Reference Manual for details on how to edit and configure an acquisition sequence. The acquisition sequence controls the instrument and autosampler. Care must be taken to use the proper acquisition method in the sequence so that the proper operating conditions are downloaded to the instrument. The acquisition sequence also provides the means for identifying raw data files. A unique ID will be assigned to each raw data file that is created as a result of the injections made throughout the analytical sequence.

12.3.1.9 Once the acquisition sequence has been properly configured and saved, the sequence can be started and analysis can begin. Refer to the specific software User's Guide and/or Reference Manual for details on how to begin an analytical sequence.

12.4 Record in the instrument run log the analytical sequence as setup in the autosampler tray. Also record the raw data file IDs which will be assigned to each injection.

12.5 Data Processing: Raw data files from either front or back columns are to be processed using the Target® software (or equivalent). Review peak integration and identification, edit if necessary, and generate quantitation reports. Perform the following procedures independently for data files obtained from each of the two analytical columns. Refer to the Target or other software User's Guide for specific details on performing these procedures.

12.5.1 Data is processed using the particular processing methods developed for Aroclor analysis. The processing method contains calibration information, integration parameters and expected retention times of analytes to be determined. Integration parameters should be developed that minimize the need for manual integration. It is imperative that samples and standards be processed using the same integration parameters. A separate, yet similar method is required for data from each column. Details for setting up and processing methods can be found in the Target® User's Guide, specifically, Chapters 6 through 9. Details on the procedures for processing data files are described in Chapter 15.

12.6 Review the processed data by looking at the Result files generated by the Target® Software. Inspect the peak integration to insure that all peaks of interest are properly integrated. Manual integrations may be performed, if necessary.

Any manual integration performed on any sample, standard, or QC sample should be made and documented as described in the most recent manual integration SOP, PGH-C-030. Review peak identification and confirm through comparison of peak retention times to target analyte retention time windows. Peaks whose retention times fall within the retention time window of a particular target analyte shall be identified as that analyte. However, the analyst may determine through overlays and comparison to the standards that peak within the retention window is not a target analyte. Details for reviewing processed results are described in Chapter 16 of the User's Guide.

12.7 Dilute and reanalyze the sample extracts if the response of a target analyte in a sample extract exceeds the limits of the initial calibration range.

12.8 If chromatographic peaks are masked by the presence of interferences, further cleanup of the sample extract is required (See SW-846 Method 3600 for guidance). Appropriate cleanup procedures include sulfur cleanup. When sample extracts are subjected to cleanup procedures, the associated method blank and LCS should be subjected to the same procedure. Should cleanup yield no improvement, dilution of the sample should be performed, thereby elevating the reporting limits for that sample.

12.9 Once peak integration and identification are acceptable, save the data file, and re-quantitate results and generate reports (electronic). Reports will include tabular results for analytes of interest and a chromatogram of the sample. Refer to Chapter 18 of the Target® User's Guide for details on generating and printing reports.

12.10 Review of reports and data.

12.10.1 When the sample reports have been printed (electronic for samples, hardcopy for calibrations), review the reports and chromatograms. Calculations of concentrations are performed by the software. These calculations are subjected to peer review to insure accuracy. Review reports for all samples from one column initially. Based upon results obtained from the first column, use the reports for samples from the second column for confirmation when necessary.

12.10.2 If the concentration of an analyte in a sample is less than the concentration of the laboratory generated reporting limit for that analyte, then the result for that analyte is reported as less than reporting limit. Data for that analyte in the sample from the second column need not be evaluated. Reporting limits are calculated using the lowest calibration level analyzed or in accordance with project requirements (only when such requirements are higher than the laboratory generated limits). Currently, the laboratory generated limit is 0.25 µg/L for aqueous samples with an initial volume of 1 liter, 16.7 µg/L for soils with an initial mass of 15 grams, 125µg/Kg for soils with an initial mass of 2 grams, 0.5 mg/L for wastes, 2.5µg for wipes. Lower reporting limits may be achieved and reported in accordance with method requirements.

12.10.3 If the concentration of analyte determined exceeds the reporting limit for that analyte, then the data from the confirmation column must be evaluated for that analyte in that sample to confirm the presence of that analyte in the sample.

12.10.4 If the analyte in question is also detected in the sample on the second column, compare the concentration determined for the analyte on this column to the reporting limit for the analyte. If the concentration exceeds the reporting limit, then the presence of that analyte in the

sample is confirmed. Report the higher of the two concentrations, unless otherwise specified by client requirements. If the relative percent difference between the concentrations determined on both columns exceeds 40%, it will be noted in the final report.

12.10.5 If the analyte is either not detected in the sample on the second column or the concentration determined for the analyte on the second column is less than the reporting limit, then the result for that analyte for that sample will be reported as less than reporting limit.

12.10.6 If samples for a particular project are to be reported with "J flagging" (estimated values between the MDL and reporting limit), then any positive value that exceeds the MDL for a given analyte on the primary column must be confirmed on the confirmation column.

12.10.6.1 If the analyte is detected on the confirmation column above the MDL for that analyte, the analyte is considered present, and the higher of the two values is reported, unless otherwise specified by the client.

12.10.6.2 If the analyte is either not detected or the result is less than the MDL for that analyte, the analyte is considered not detected.

12.10.7 After processing and analyst review are completed, the data are ready for reporting.

12.11 Reporting of results

12.11.1 Include all pertinent information associated with analysis of samples from a particular project in the final report. This information includes, but is not limited to any comments about the analysis describing problems and/or non-conformances and QC failures.

12.11.2 Enter results into the Laboratory Information Management System (LIMS) for each sample in the project.

13. Calculations

13.1 Calibration Factors:

$$CF = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

13.2 Mean Calibration Factor

$$\overline{CF} = \frac{\sum_{i=1}^{n} CFi}{n}$$

Where n = the number of standards analyzed
CF = the calibration factor for each standard

13.3 Percent Relative Standard Deviation (%RSD)

$$StdDev = \sqrt{\frac{\sum_{i=1}^{n} (CFi - \overline{CF})^2}{n-1}}$$

$$\%RSD = \frac{StdDev}{\overline{CF}} * 100$$

13.4 Calibration Factor % Difference (%D)

$$\%Difference = \frac{CF - \overline{CF}}{\overline{CF}} * 100$$

13.5 Relative Percent Difference (%RPD):

$$RPD = \frac{|A - B|}{(A + B)/2} x100$$

Where: RPD = Relative Percent Difference
A = First Column Value
B = Second column Value

13.6 Concentration for Aqueous Samples

$$Concentration\ (\mu g/L) = \frac{(A)\ (Vt)\ (D)}{(CF)\ (Vi)\ (Vs)}$$

Where:

(A) = Response of analyte peak
(CF) = Average Calibration Factor for analyte
(D) = Dilution Factor
(Vi) = Volume of extract injected (uL)
(Vt) = Volume of total extract (uL)
(Vs) = Volume of water extracted (mL)

13.6.1 The final concentration of PCB Aroclor(s) in the sample is determined by averaging the five concentrations determined for each of the five peaks chosen for quantitation of a given Aroclor.

13.7 Concentration for Non-aqueous Sample

$$Concentration\ (\mu g/Kg) = \frac{(A)\ (Vt)\ (D)(1000)}{(CF)(Vi)\ (Ws)}$$

Where:

(A) = Response of analyte peak
(CF) = Average Calibration Factor for analyte
(D) = Dilution Factor
(Vi) = Volume of extract injected (µL)
(Vt) = Volume of total extract (mL)
(Ws) = Weight of solid extracted (g)

13.1 The final concentration of PCB Aroclor(s) in the sample is determined by averaging the five concentrations determined for each of the five peaks chosen for quantitation of a given Aroclor®.

13.2 Matrix Spike/Matrix Spike duplicate and LCS percent recovery:

$$\% \text{ Recovery} = \frac{C_{ss} - C_s}{S} \times 100$$

Where:

C_s = Concentration of the source sample
C_{ss} = Concentration of the spiked sample
S = Amount spiked

14. Quality Control

14.1 Each batch of samples will have an associated Method Blank (MB), Laboratory Control Sample (LCS), and a Matrix Spike/Matrix Spike Duplicate (MS/MSD) if there is sufficient sample volume.

14.2 Matrix spike and matrix spike duplicates should be within laboratory established QC limits. See Table 1 of this procedure for laboratory generated acceptance limits. If unacceptable results are obtained, an evaluation of the LCS must occur to determine if sample matrix is a possible interference. Also, the Matrix Spike and Matrix Spike Duplicate recoveries must be in agreement (i.e. the relative percent difference (RPD) must not exceed laboratory QC limits of ±25% for water and soil samples). If the RPD is unacceptable, the samples must be evaluated for the cause and the MS/MSD samples should be reanalyzed or re-extracted if possible or flag and narrate data. If both MS and MSD %recovery results are outside QC limits this confirms matrix interference, flag, narrate and report data.

14.2.1 Method blanks must be analyzed and evaluated for contamination. If a recovery of contaminant is found in the Method Blank above the reporting limit (1/2 the reporting limit for client specific requirements), all samples in that extraction batch must be re-extracted.

14.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Surrogate recoveries in water and in solids should be within laboratory established QC limits listed in Table 1.

14.4 Include a calibration verification standard (CVS) after each group of 20 sample it is recommended that a calibration standard be included after every 10 samples to minimize the number of repeat injections, in the analysis sequence as a calibration check. The calibration factors for the Aroclor and surrogates must be within 15% for Method 8082 and 20% for Method 8082A of the initial calibration. When the CVS is out of the acceptance window, the laboratory should stop analyses and take corrective action as outlined in Section 15 of this procedure.

14.5 Corrective Actions for Out-Of-Control Data

14.5.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.5.2 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.5.2.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.5.3 Matrix Spike Recovery (MS) – If the Matrix Spike recoveries do not meet the acceptance criteria, the batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the spike recovery is not within the 25% RPD, a note is included in LIMS.

14.5.4 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.5.5 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report

15. Method Performance

15.1 Aroclor analysis method performance is achieved through the analysis of MDLs, LOD verifications, semi-annual Performance Evaluation samples, and in-house laboratory Quality Control samples (MB, LCS, MS/MSD, and surrogates in all extracted samples).

15.2 Initial calibration, Aroclors and surrogates, %RSD $\leq$ 20%, a correlation coefficient of $r \geq 0.99$ or coefficient of determination $r^2 \geq 0.99$ for each analyte.

15.2.1 ICV recovery must be within 80-120%.

15.3 Continuing calibration check: Aroclors and surrogates, %D $\leq$ 15% for Method 8082 and %D $\leq$ 20% for Method 8082A for each Aroclor.

15.4 Extraction Method Blanks may not equal or exceed the reporting limit for each Aroclor® (1/2 the reporting limit for client-specific requirements).

15.5 Aroclor target recoveries in LCS and MS/MSD extracts must be within laboratory determined acceptance windows listed in Table 1 for each Aroclor.

15.6 TCMX and/or DCB surrogate recoveries in all extracts must be within laboratory determined acceptance windows listed in Table 1.

15.7 Sulfur peak(s) resolved in samples shall be minimized through TBA clean-up of the affected samples followed by subsequent sample reanalysis.

15.8 Corrective Actions for Failed Calibration Data and Out-of Control Data

15.8.1 Failed Calibration

15.8.1.1 Check calculations and concentrations to confirm that they are correct and no errors have been made. If errors are found, re-calculate the data. If no errors are evident or the correction of the error does not alleviate the problem, proceed with 2.

15.8.1.2 Confirm chromatographic peak identification and determine if the analytes have been identified correctly. Re-identify the peak(s) or analyte(s) in question should a mis-identification be discovered. If the analytes have been identified properly or if there is still a problem after re-identification, proceed with 15.8.1.5.

15.8.1.3 Reanalyze a fresh aliquot of the standard in question. If reanalysis meets the acceptance criteria, analysis may resume. If the reanalysis of the standard still fails to meet the acceptance criteria, proceed with 15.8.1.4.

15.8.1.4 Perform one or more of the applicable maintenance procedures listed in Section 8.2.5.1 of SW-846 Method 8000B or in section 9.2.5 of 8000C and analyze a fresh aliquot of the standard in question. If the standard meets the acceptance criteria analysis may continue. If the standard still does not meet the criteria, proceed with 15.8.1.5.

15.8.1.5 Perform one or more of the applicable maintenance procedures listed in section 8.2.5.2 of Method 8000B or 9.2.5 of 8000C. Recalibration is automatically necessary when one of these procedures is preformed. Recalibrate the system.

15.8.2 Failed surrogate or spike criteria

15.8.2.1 Begin with Section 15.8.1.1-3. If recoveries still do not meet the acceptance criteria, proceed with this section.

15.8.2.2 Re-check the calibration data to confirm the problem is not due to an out-of-control calibration. If this does not remedy the problem, proceed with 15.8.2.3.

15.8.2.3 Re-extract and reanalyze the affected samples. If the problem persists, the cause may be matrix related. The department lead analyst and/or supervisor will be made aware of the circumstances, and the situation will be described in the final report.

15.8.2.4 If re-extraction yielded the same results, or if reextraction is impossible due to lack of sample, it may be necessary to re-sample. This should be determined by the Project Manager and the client.

15.8.3 Blank Contamination

15.8.3.1 Begin with Section 15.8.1.1-3. If recoveries still do not meet the acceptance criteria, proceed with this section.

15.8.3.2 If the contaminants which were found in the blank are not present in any samples, samples may not need to be re-extracted and reanalyzed. This will be determined by the Project Manager and/or client.

15.8.3.3 If the contamination is present throughout the batch of samples, reextraction and reanalysis will be required.

15.9 Any data that are considered out of control (suspect) or unacceptable will be appropriately flagged as such and qualified in the analytical report.

15.10 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.11 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.12 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 All reagent, solvent, standard, and extract containers are tightly sealed when not in immediate use. If a solvent or extract spill does occur, the spill is contained with paper towel, or other appropriate material. All waste materials, expired

standards and samples are placed into a properly designated and labeled waste container.

16.2 An attempt is made to minimize the quantity of hexane waste generated that is associated with the analysis. All Aroclor standards, QCs, and sample extracts are dispensed into 300 or 500 µL glass inserts that fit into 2mL autosampler vials. The remaining ~4.6mL of sample extract volume is stored in the flammable sample refrigerator until the extract is permitted to be disposed. The "spent" 400µL of injected hexane extract is either dispensed into an appropriate hexane waste container, or allowed to evaporate in a fume hood, prior to proper disposal of the waste glass. The remaining hexane extract is dispensed into the appropriate hexane waste container prior to proper disposal of this waste glass.

17. References

17.1 USEPA, SW-846, Determinative Chromatographic Separations. Method 8000C. Revision 3. March 2003.

17.2 Polychlorinated Biphenyls (PCB) by Gas Chromatography. EPA SW846 Series 8082. Revision 1. December 1996.

17.3 Polychlorinated Biphenyls (PCB) by Gas Chromatography, EPA SW846, Final Update IV, Method 8082A, Revision 1, February 2007.

17.4 Target: Chromatographic Analysis Software User's Guide. (1997 Target Revision 3.4) Thru-Put Systems, Inc. Orlando, FL.

17.5 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.6 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.7 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.8 SOPs PGH-O-028 Separatory Funnel Extraction, current version.

17.9 SOP PGH-O-022 Microwave Extraction, current version.

17.10 SOP PGH-O-011, Waste Dilution Extraction, current version.

17.11 SOP PGH-M-016, Percent Moisture, current version.

17.12 SOP PGH-C-026, Control Charts, current version.

17.13 SOP PGH-Q-030, Manual Integrations, current version.

17.14 SOP PGH-C-032, Support Equipment, current version.

17.15 SOP PGH-Q-035, MDL-LOD, current version.

17.16 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.17 SOP PGH-Q-038, Laboratory Equipment, current version.

17.18 SOP PGH-Q-040, Audits, current version.

17.19 SOP PGH-Q-039, Corrective Action, current version.

17.20 SOP S-ALL-Q-020, Training, current version.

17.21 SOP S-ALL-Q-028, Lab Track, current version.

17.22 SOP PGH-C-027, DI Water, current version

18. Tables, Diagrames, Flowcharts, Appendices, etc.

Table 1 - Control Limits: MS/LCS and Surrogate

Appendix 1 - Determination of Retention Time Windows

Appendix A – Example Chromatographic Pattern for:

Aroclor – 1016
Aroclor – 1221
Aroclor – 1232
Aroclor – 1242
Aroclor – 1248
Aroclor – 1254
Aroclor – 1260

19. Instrument Maintenance

19.1 In order to keep the instrument running at peak performance, it will be necessary from time to time to perform some type of maintenance on the instrument. All maintenance performed on a particular instrument will be documented in the Instrument Maintenance Logbook for that instrument. This documentation will include not only the actual maintenance performed, but also the reason the maintenance is deemed necessary and the results of the maintenance (i.e. Did the maintenance resolve the issue).

19.2 Injection port

19.2.1 Many issues with chromatographic performance can be attributed to a dirty or contaminated injection port. A mispositioned column (i.e., too much or too little column projecting past the column nut ferrule) can also cause poor performance. Symptoms of injection port issues include, but are not limited to, Endrin/DDT breakdown (pesticide analysis), small, broad peaks, peak tailing, peak fronting, noisy baseline, ghost peaks, and retention time shifts.

19.2.2 The issues of breakdown, noisy baseline, or ghost peaks can usually be resolved by replacing the glass wool in the injection port liner. If there is no wool in the liner or replacement of the wool fails to resolve the issue, the liner itself should be replaced. In most cases this will resolve the issue. If the issue persists, the injection port itself should be cleaned with solvent.

19.2.3 Peak tailing and fronting are typically a result of poor column placement in the injection port. The tip of the column should extend 3 to 5 mm beyond the tip of the ferrule in the column nut. When tailing or fronting occurs, the positioning of the column should be checked and modified if needed.

19.2.4 Retention time shifts are generally a result of loose connections or a cored injection port septum. Tightness of column nuts, adapter nuts and septum caps should be checked and tightened as needed. If the septum shows signs of coring, it should be replaced. A cored septum may also result in ghost peaks as unvolatilized solvent can become trapped in the hole left by the core.

19.2.5 The injection port septum should be replaced every time any injection port maintenance is performed.

19.3 Detectors

19.3.1 Through continued use, the ECDs that are employed in this procedure can become dirty and/or contaminated, resulting in high baselines, noisy baselines and non linear response.

19.3.2 Optimal operating signals for the ECDs used in this procedure are <100 for the typical cells and <1000 for the micro ECDs. Response may be acceptable above these values, but as they continue to rise, performance will deteriorate.

19.3.3 When results from the ECDs become erratic, the detectors should be removed from the instrument and sent to an authorized vendor for cleaning and/or foil replacement.

19.4 Columns

19.4.1 Through continued use, contaminants can deposit on the front end of the column causing erratic performance including noisy baseline, small broad peaks, and poor resolution.

19.4.2 The front end of the column should be clipped removing 2 to 5 inches to resolve these problems.

19.4.3 Eventually, the gains in performance achieved from clipping the column will become outweighed by the loss of resolution due to the shorter column. At this point the column should be replaced.

19.4.4 After prolonged use, due to the continual heating and cooling of the column, the column will begin to lose stationary phase resulting in poor resolution and increased column bleed. When resolution or column bleed becomes unacceptable, the column should be replaced.

20. Method Modifications

20.1 For Method 8082: When evaluating the 1660 CCV against the 15% D criteria, if one or more of the individual Aroclor peaks exceeds 15%, the average %D of all five peaks is evaluated. If the average %D of all five peaks is less than 15 %, the verification is considered acceptable.

20.2 The laboratory uses in house generated control limits, not 80-120%, for the QC reference samples (LCSs) that are analyzed at a minimum of 1 per 20 samples or 1 per batch if fewer than 20 samples.

20.3 The laboratory uses the dual column approach and will report data from one column when criteria are not met from the second column.

20.4 Method 8000C requires reporting the lower of the two results. Pace Pittsburgh Laboratory will report the higher of the two results unless otherwise instructed by the client.

21. Revisions

Document Number	**Reason for Change**	**Date**
WI-PGH-O-038-0	1. Created Project Specific Work Instruction using PASI-PGH SOP PGH-O-009-10 for the Sparrow Point project that has Sections: 11.1.5.1 and 13.1 modified to use peak area only. Section 14.2 Changed Appendix C reference to Table 1.	07Jul2015

Table 1
Control Limits, MS/LCS and Surrogate

Compound	Control Limits (%) Water	Control Limit Solid (%)
MS/LCS		
Aroclor 1016	51-97	40-100
Aroclor 1221	42-109	44-99
Aroclor 1232	56-104	39-107
Aroclor 1242	43-102	40-107
Aroclor 1248	53-98	40-102
Aroclor 1254	45-119	42-110
Aroclor 1260	47-75	41-109
Aroclor 1262	55-145	55-145
Aroclor 1268	55-145	55-145
Surrogate (%)		
Decachlorobiphenyl (DCB)	10-110	10-115
Tetrachlor-m-xylene (TCMX)	29-105	30-107
Note: Control limits are calculated based on laboratory data. Limits are subject to change.		

Appendix No. 1
Determination of Retention Time Windows
EPA Method 8000C (Section 11.6)

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC and HPLC methods that do *not* employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

The following subsections describe one approach that may be used to establish retention time windows for GC methods. Other approaches may be employed, provided that the analyst can demonstrate that they provide performance appropriate for the intended application.

1. Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as Aroclors) over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

2. Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

3. If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

4. The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period or 0.03 minutes, whichever is greater. (If the default standard deviation in Sec. 11.6.3 is employed, the width of the window will be 0.03 minutes.)

5. Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

6. The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

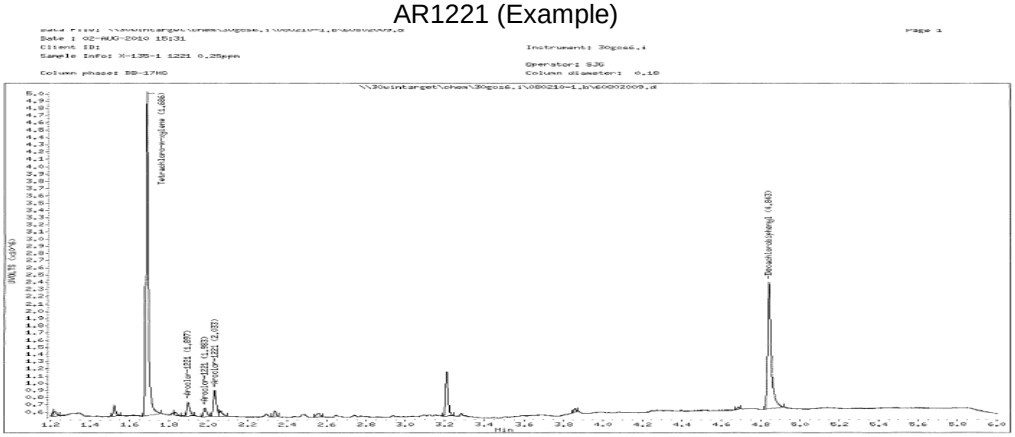
7. If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst.

8. The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention

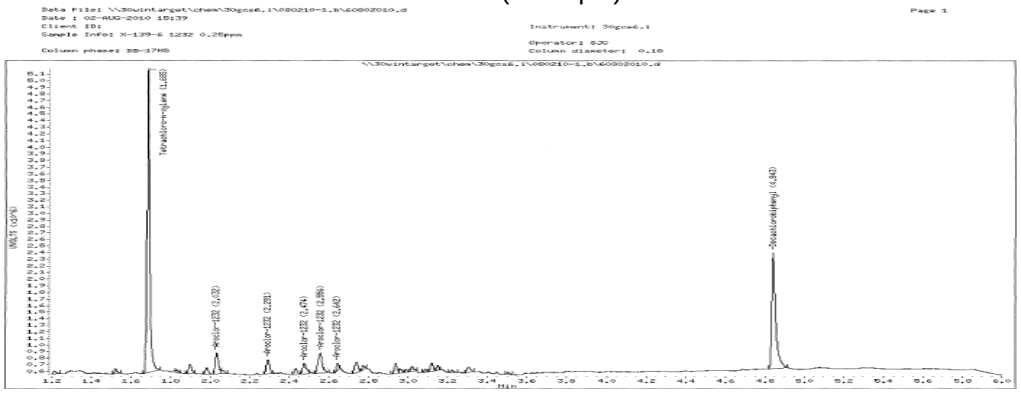
time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

Appendix A
Aroclor Chromatogram Examples

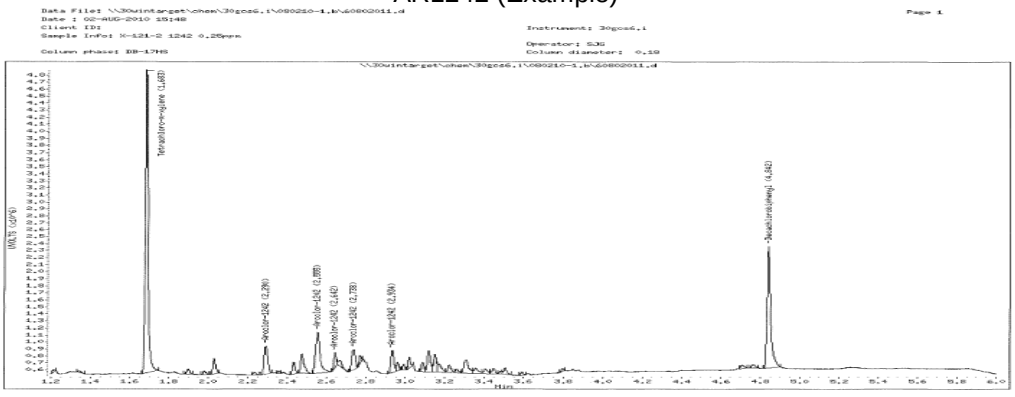
AR1221 (Example)



AR1232 (Example)

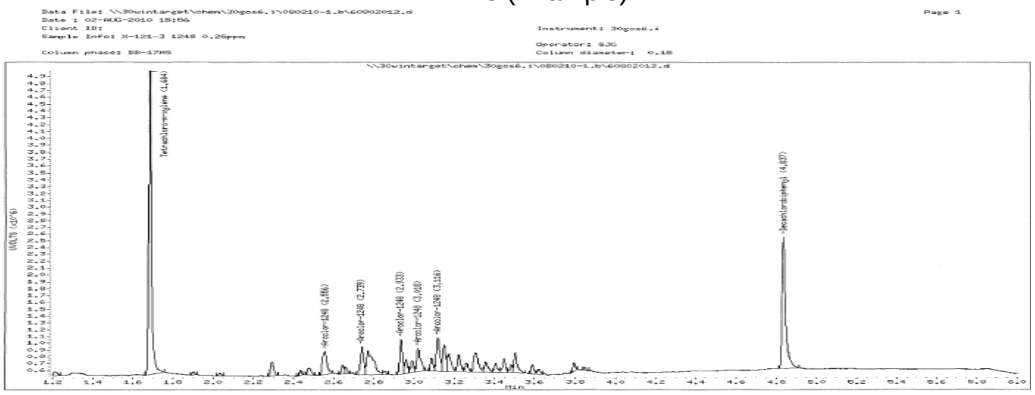


AR1242 (Example)

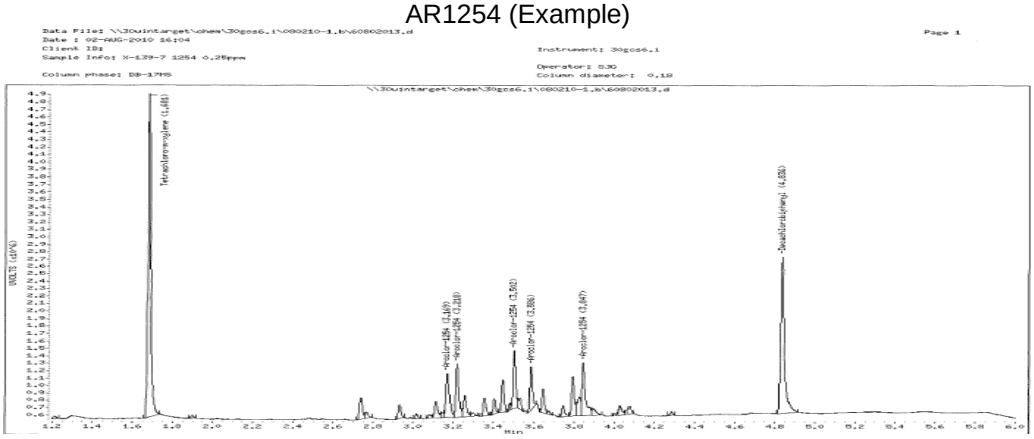


PCB Chromatogram Examples

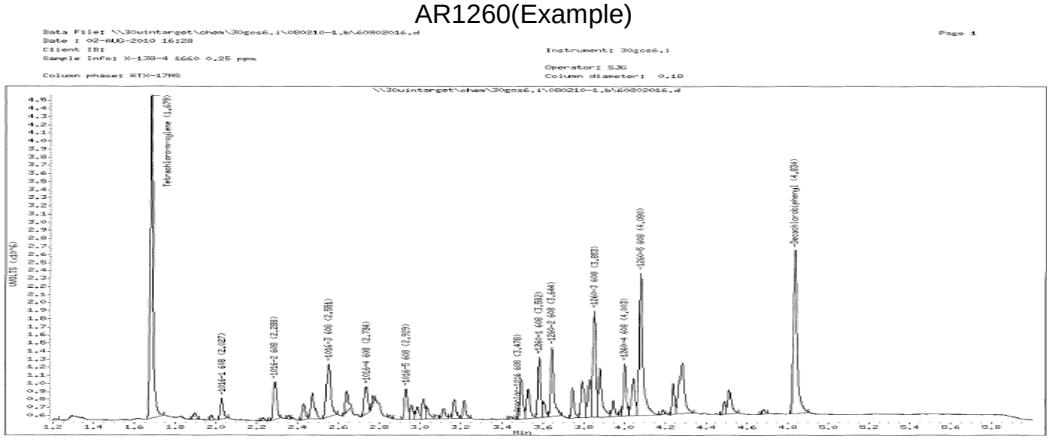
AR1248 (Example)



AR1254 (Example)



AR1260(Example)



STANDARD OPERATING PROCEDURE

ANALYSIS OF PCBS BY GC/MS

Reference Methods: EPA Method 680

SOP Number:	S-NY-O-040-rev.08
Effective Date:	08/14/15
Supersedes:	S-NY-O-040-rev.07

APPROVALS

Assistant General Manager	08/14/15 Date
Quality Manager	08/14/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

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1. Purpose/Identification of Method

1.1. This Standard Operating Procedure (SOP) is used to determine Polychlorinated Biphenyls (PCBs) by GC/MS in liquids, waters, solids, and sediments, and TO-4A and TO-10A polyurethane foam (PUF) air cartridges.

2. Summary of Method

2.1. Samples are extracted with pesticide-grade solvents using SW-846 Methods 3510C, 3540C, TO-4A, or TO-10A. Refer to SOP S-NY-O-141, S-NY-O-323, S-NY-O-151, and S-NY-O-241 current revisions respectively for further details. The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of cleanup techniques. The sample is then analyzed by injecting the extract onto a gas chromatographic system and the PCBs detected by a mass spectrometer.

2.2. This SOP provides detailed instructions for GC/MS conditions, calibration, and analysis of PCBs by GC/MS.

2.3. Sample extract components are separated with capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization mass spectrometry (MS). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential. Selected-ion-monitoring (SIM) data will be acquired.

2.4. A Varian Saturn Ion Trap GC/MS is used to perform this analysis. Varian uses a proprietary field-modulated Wave-Board technology to selectively trap only those ions of interest. Background ions are not stored. This allows for a much cleaner spectrum and a considerable increase in sensitivity since the trap's capacity is dedicated to these ions of interest. Additionally, the selected storage mass range (Method 680 requires scanning ions across 5 mass ranges) is time programmable so that many different target analytes can be selectively stored relative to the background matrix. Varian refers to this mode of operation as Selected Ion Scanning (SIS) mode. SIS is Varian's term for Selected Ion Monitoring (SIM) common to most other mass spectrometers. SIS allows the Saturn Ion Trap to store many more masses than traditional SIM techniques without a corresponding loss of sensitivity. The more common term SIM (versus SIS) will be used throughout the SOP for ease of reference.

2.5. Two surrogate compounds are added to each sample before sample preparation; these compounds are 2,4,5,6-Tetrachloro-m-xylene (TCMX) and 13C labeled decachlorobiphenyl (D[$^{13}C_{12}$]BP). Two internal standards, chrysene-d12 and phenanthrene-d10, are added to each sample extract before GC/MS analysis and are used to calibrate MS response. Each concentration measurement is based on an integrated ion abundance of one characteristic ion.

2.6. PCBs are identified and measured as isomer groups or homologs (i.e., by level of chlorination). A concentration is measured for each PCB isomer group total; total PCB concentration in each sample extract is obtained by summing isomer group concentrations. Nine selected PCB congeners are used as calibration standards, and one internal standard (chrysene-d12) is used to calibrate MS response to PCBs, unless sample conditions require the use of the second internal standard (phenanthrene-d10).

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analysis of samples by method 680.

3.2. This method is restricted to use by or under the supervision of analysts experienced in the operation of a gas chromatograph/mass spectrometer and the interpretation of mass spectral data.

3.3. **Parameters**: The existence of 209 possible PCB congeners makes impractical the listing of the Chemical Abstracts Service Registry Number (CASRN) for each potential method analyte. Because PCBs are identified and measured as isomer groups (i.e., by level of chlorination), the non-specific CASRN for each level of chlorination is used to describe method analytes:

ANALYTE	FORMULA	CAS NUMBER
PCBs		
Monochlorobiphenyls	$C_{12}H_9Cl$	27323-18-8
Dichlorobiphenyls	$C_{12}H_8Cl_2$	25512-42-9
Trichlorobiphenyls	$C_{12}H_7Cl_3$	25323-68-6
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	26914-33-0
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	25429-29-2
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	26601-64-9
Heptachlorobiphenyls	$C_{12}H_3Cl_7$	28655-71-2
Octachlorobiphenyls	$C_{12}H_2Cl_8$	31472-83-0
Nonachlorobiphenyls	$C_{12}HCl_9$	53742-07-7
Decachlorobiphenyls	$C_{12}Cl_{10}$	2051-24-3

4. Applicable Matrices

4.1. This method is applicable to all liquids, waters, solids, sediments, and polyurethane foam (PUF) air cartridge samples.

5. Limits of Detection and Quantitation

5.1. The method detection limit studies and current reporting limits are maintained by the Quality Manager.

6. Interferences

6.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

6.2. Glassware must be scrupulously cleaned.

6.3. High purity solvents and reagents must be used.

6.4. For PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences (refer to the applicable extraction SOPs for extract cleanup procedures). Capillary column GC retention time and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs. With the isomer group approach, coeluting PCBs that contain

the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms. This interference problem is obviated by rigorous application of the identification criteria described in this method.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Water Samples:

7.1.1. Samples must be collected in clean glass containers.

7.1.2. All samples must be iced or refrigerated at 0-6°C from the time of collection until extraction. If the samples will not be extracted within 72 hours, use either sodium hydroxide of sulfuric acid to adjust the pH to within a range of 5 to 9.

7.1.3. All samples must be extracted within seven days of collection and completely analyzed within 40 days of extraction.

7.2. Soil/Sediment Samples:

7.2.1. All samples should be collected in glass containers and iced or refrigerated at 0-6°C from the time of collection until extraction.

7.2.2. All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.2.3. Store sample extracts at 0-6°C protected from light in sealed screw top vials equipped with un-pierced septa.

7.3. Air (PUF) Samples:

7.3.1. All samples should be collected as per EPA method TO-4A, TO-10A, and the client's Field Sampling and Analysis Plan as applicable.

7.3.2. Samples should be stored at >0-6°C degrees Celsius.

7.3.3. Samples must be extracted within 7 days of collection and analysis must be performed within 40 days of extraction.

7.3.4. Store sample extracts 0-6°C protected from light in sealed screw top vials equipped with un-pierced septa.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

8.2. **Initial Calibration Solution (ICAL):** A solution of method analytes used to calibrate the mass spectrometer response.

8.3. **Congener Number:** Throughout this method, individual PCBs are described with the number assigned by Ballschmiter and Zell (2). (This number is also used to describe PCB Congeners in catalogs produced by Ultra Scientific, Hope, RI).

8.4. **Internal Standard (IS):** A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

8.5. **Method Blank (MB):** An aliquot of water or other blank matrix spiked with surrogate solution and prepared with each sample batch. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or extraction apparatus.

8.6. **Surrogate Compound (SURR):** Compounds, which are chemically similar to the analytes, which behave like the analytes during preparation and analysis, but do not interfere with the analysis of the analytes. Used to determine the proficiency of the preparation and analysis of samples.

8.7. **Laboratory Control Sample (LCS) or Quality Control (QC) Check:** A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst.

8.8. **Matrix Spike (MS):** Prepared by adding a known amount of analyte to the sample matrix prior to sample preparation. The analysis of a matrix spike is used to determine the accuracy of the analysis.

8.9. **Matrix Spike Duplicate (MSD):** Prepared in the same manner as the matrix spike. The analysis of a matrix spike/matrix spike duplicate is used to determine the precision of the analysis.

8.10. **Window Defining Mix (WDM):** Analyzed to provide a check on retention time for the four PCB congeners used to established retention time segments for SIM data acquisition.

8.11. **Continuing Calibration Verification Standard (CCV):** This is a mid-level calibration standard that must be run at the beginning and end of every 12 hour sequence, after the tuning standard.

8.12. **Laboratory Solvent Blank (LSB):** A sample consisting of solvent(s) and/or reagents that is carried through all subsequent extraction and analytical procedures without the addition of surrogate or internal standard compounds.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Gas Chromatograph: Varian 3800 GC and a 1079 split/splitless temperature programmable injector. See Tables 2 and 3 for temperature programs.

9.2. Mass Spectrometer: Varian Saturn 2000 ion trap mass spectrometer and SIM data acquisition system. The data system is equipped with software capable of acquiring data for multiple groups of ions, and allows automated and rapid changes of the set of ions being monitored. The SIM program is capable of acquiring data for five groups (or mass ranges) each consisting of ≤ 27 ions each. The times spent monitoring ions during sample analyses is the same as the times used when calibration solutions were analyzed. The MS produces a mass spectrum meeting all criteria for ≤ 20ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.

9.3. Auto sampler: Varian 8400.

9.4. Processing Software: Thru-Put Target™ Software and automated ion extraction software.

9.5. Column: 30m x 0.25mm ID, 0.25µm film thickness, J&W DB-XLB (122-1232)..

9.6. Ferrules: graphite/vespel, SGE (072663) or equivalent; graphite, Varian (03-925342-01).

9.7. Injector septa: 11mm, Supelco (20654) or equivalent.

9.8. Injector liner: SGE (092245).

9.9. Syringes: 10µL-1000µL.

9.10. Class A volumetric flasks: Various sizes.

9.11. Auto sampler vials: 1.8mL, amber snap top vials, SRI (501-302) or equivalent.

9.12. Auto sampler caps: snap cap, Microliter, (11-0051N-B) or equivalent.

9.13. Auto sampler vials: 1.8mL, clear screw top with cap, Lab Supply, (402105-540) or equivalent.

9.14. 350µL Flat Bottom Inserts, SRI (200-670).

9.15. Disposable Pasteur pipettes.

10. Reagents and Standards

10.1. Stock Standard Solutions – All standards are purchased as certified solutions from various suppliers and stored at –10°C to –20°C and protected from light.

10.2. n-Hexane**:** High purity solvent, Burdick & Jackson.

10.3. Methanol: High purity solvent, Burdick & Jackson.

10.4. Internal Standards: Chyrsene-d12, 2000µg/mL, (ATS-120) and Phenanthrene-d10, 1000µg/mL, (IST-230), Ultra Scientific.

10.4.1. To a 25mL volumetric flask containing 20mL of n-hexane, add 500µL of Chyrsene-d12 and 1000µL Phenanthrene-d10. Using n-hexane, set to volume, cap, and invert three times. Transfer into a properly labeled bottle.

10.5. 2,4,5,6-Tetrachloro-m-xylene (TCMX) Surrogate Standard Mixture: 2000µg/mL, (IST-440) Ultra Scientific.

10.5.1. TCMX Surrogate at 20µg/mL: To a 100mL volumetric flask containing 99mL of methanol, add 1.0mL of TCMX surrogate solution at 2000µg/mL. Cap and invert three times. Transfer into a properly labeled bottle.

10.5.2. TCMX Surrogate at 0.5µg/mL: To a 100mL volumetric flask containing 97.5mL of methanol add 2.5mL of TCMX surrogate solution at 20µg/mL. Cap and invert three times. Transfer into a properly labeled bottle.

10.5.3. TCMX Surrogate at 0.2µg/mL: To a 25mL volumetric flask containing 24.75mL of methanol add 250µL of TCMX surrogate solution at 20µg/mL. Cap and invert three times. Transfer into a properly labeled bottle.

10.6. Decacholorbiphenyl [13C labeled] (D[$^{13}C_{12}$]BP) Surrogate Standard Mixture: 50µg/mL, Wellington Laboratories (MBP-209).

10.6.1. D[$^{13}C_{12}$]BP Surrogate Solution at 5.0µg/mL: To a 10mL volumetric flask containing 9.0mL of methanol, add 1.0mL of D[$^{13}C_{12}$]BP surrogate solution at 50µg/mL. Cap and invert three times. Transfer into a properly labeled bottle.

10.6.2. D[$^{13}C_{12}$]BP Surrogate Solution at 1.0 µg/mL: To a 10mL volumetric flask containing 9.8mL of methanol, add 0.20mL of D[$^{13}C_{12}$]BP surrogate solution at 50µg/mL. Cap and invert three times. Transfer into a properly labeled bottle.

10.7. PCB Window Defining Mixture (WDM): 2.5µg/mL, AccuStandard (C-WDM).

10.8. Decafluorotriphenylphosphine Stock Standard (DFTPP): 250µg/mL, Ultra Scientific (IST-340).

10.8.1. DFTPP at 10µg/mL: To a 25mL volumetric flask containing 20mL of n-hexane add 1000µL of the stock solution. Using n-hexane set to volume, cap and invert three times. Transfer into a properly labeled bottle.

10.9. Standards: Retention Time Calibration Mix, (CB-682MN), Concentration Calibration Mix, (CB-681MN), Ultra Scientific.

10.9.1. 680 Calibration Stock Solution: To a 10mL volumetric flask, add 5.5mL of n- hexane. Then add 1000µL of both calibration standards and 2500 µL TCMX Surrogate at 20µg/mL. Set to volume with n-hexane. Transfer into a properly labeled 4 dram vial.

10.9.2. Prepare the 680 calibration curve as shown in Table 5.

10.10. 680 Calibration Standard (for Calibration Verification Standard): PCB Isomer Calibration Mix (M-680A), Retention Time Calibration Standard (M-680-RT), TCMX (M-8082-SS-10X) AccuStandard and D[$^{13}C_{12}$]BP Surrogate Solution (50 µg/mL), Wellington.

10.10.1. Calibration Verification Stock Standard: To a 10mL volumetric flask, add 7.0mL of n-hexane. Then add 1000µL of both calibration standards and 50µL TCMX Surrogate at 1000µg/mL. Set to volume with n-hexane. Transfer into a properly labeled 4 dram vial.

10.10.2. Calibration Verification Standard: To a 10mL volumetric flask add 5.0mL of n- hexane. Then add 2000µL of the Calibration Verification Stock Standard and 1000µL D[$^{13}C_{12}$]BP Surrogate Solution. Set to volume with n-hexane. Transfer into a properly labeled 4 dram vial.

10.11. 680 Spike Standard: To a 5.0mL volumetric flask, add 3.0mL of methanol. Then add 1000µL of the Concentration Calibration Mix, (CB-681MN), Ultra Scientific. Set to volume with methanol. Transfer into a properly labeled 4 dram vial. **Note: Record the preparation of all standards in the Semi-Volatiles Standard Preparation Book and store away from direct light at 0-6°C in Refrigerator #14.**

11. Calibration and Standardization

11.1. GC/MS Tuning:

11.1.1. At the beginning of each 12 hour shift the GC/MS system must pass performance criteria for DFTPP listed in Table 1.

11.1.2. Inject 2.0µL of the 10µg/mL DFTPP solution using the auto sampler.

11.1.3. Any scan across the peak may be used to meet the criteria as listed in Table 1. Averaging scans is also allowed as an option for meeting the criteria. Always use background-subtracted spectra. Use the Target™ software to evaluate the tuning compound. A DFTPP injection must be performed every 12 hours prior to the analysis of any blanks, samples or standards.

11.2. The WDM is analyzed immediately after the tune but before the CCV. Absolute retention times of PCB congeners #77, #104, #202, and #189 should not vary by more than ±10 s from one analysis to the next. (Retention time reproducibility is not as critical for congeners #1 and #209 as for the other four congeners, which are used to determine when ion sets are changed).

11.3. Initial Calibration:

11.3.1. Set up your instrument using the parameters listed in Table 3. Prepare the seven calibration standards as described in Table 5. Using a 500µL syringe measure 200µL of the standard and transfer to a snap-cap vial equipped with a 350µL flat bottom insert. Repeat this for each of the seven standards. Add 4µL of IS to each standard. Inject 2.0µL of each standard using the same instrument parameters as will be used for samples.

11.3.2. Response factors (RFs) are calculated for each target analyte relative to the chrysene-d12 internal standard.

11.3.3. All target analytes must have an RSD $\leq$ 20%. If a situation arises where the RSD for one or more analytes exceeds 20% corrective action must be taken and the calibration curve must be re-analyzed.

11.3.4. Data will be acquired with the five ion sets (≤ 27 ions each) exhibited in Table 12.

11.3.5. The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the retention times (scan numbers) of the retention time congeners (WDM).

11.3.6. Begin data acquisition with Ion Set #1 before elution of PCB congener #1, the first eluting Cl_1 -PCB. Stop acquisition with Ion Set #1 and begin acquisition with Ion Set #2 (approximately 10 seconds) before elution of PCB congener #104, the first eluting Cl_5 -PCB. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 (approximately 10 s) after elution of PCB congener #77, the last eluting Cl_4 -PCB. Stop acquisition with Ion Set #3 and begin acquisition with ion Set #4 (approximately 10 s) before elution of PCB congener #202, the first eluting Cl_8 -PCB. Stop acquisition with Ion Set #4 and begin acquisition with Ion Set #5 (approximately 10 s) after elution of PCB congener #189, the last eluting Cl_7-PCB, stop acquisition of Ion Set #5 after Cl_{10}-PCB elution.

11.4. Performance Criteria:

11.4.1. The following criteria must also be met: Baseline separation of PCB congener #87 from congeners #154 and #77 which may coelute; signal/noise ratio of ≥ 5 for m/z 499 of PCB congener #209, Cl_{10} -PCB, and for m/z 241 of chrysene-d12; an abundance of ≥ 70% and≤ 95% of m/z 500 relative to m/z 498 for congener # 209, Cl_{10} –PCB.

11.5. Calibration Verification:

11.5.1. The initial calibration must be verified at the beginning and end of each 12 hour period by injecting the mid-point level standard using the same conditions as the initial calibration.

11.5.2. For an acceptable CCV, the measured RF for each analyte/surrogate compound must be within ±20 % of the mean value calculated during initial calibration. If not, remedial action must be taken; recalibration may be necessary.

11.5.3. The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time of any internal standard changes by more than 30 seconds from that in the mid-point standard of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.4. Determine that neither the area measured for m/z 240 for chrysene-d12 nor that for m/z 188 for phenanthrene-d10 has decreased by more than 30% from the area measured in the most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration. If the area for any internal standards fails criteria, the mass spectrometer must be inspected for malfunctions and corrections must be made, as required.

11.5.5. Demonstrate and document acceptable reproducibility of absolute retention times of appropriate PCB retention time congeners by analysis of the PCB Window defining mixture.

12. Procedure

12.1. Set up the method parameters for the GC (Tables 2 and 3).

12.2. Inject 2.0µL of the 10µg/mL DFTPP solution using the auto sampler.

12.3. **Sample Analysis:**

12.3.1. Samples can be analyzed up to 12 hours after a valid tune. A WDM, a beginning and an ending CCV must be included in that time period. Acquire mass spectral data with SIM conditions. Use the same data acquisition time and MS operating conditions previously used to determine response factors.

12.3.2. Before samples, blanks, or matrix spikes can be analyzed they must be spiked with internal standard. Prepare snap-cap auto sampler vials with limited volume inserts. Measure out 200µL of extract into the auto sampler vial and add 4µL of IS per 200µL of extract. Inject 2.0µL of each blank, QC sample, standard, or sample with the same auto sampler parameters.

12.3.3. Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately. In addition, any individual PCB analyte amount that exceeds the high level calibration standard of the calibration curve will require dilution and re-analysis of the extract to place that analyte within the calibration range.

12.3.4. For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

12.4. **Identification Procedures:**

12.4.1. Using the ions shown on Tables 12 and 13 for PCBs examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, and PCBs for each isomer group.

12.4.2. SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions for the quantitation and confirmation ions for each PCB isomer group.

12.4.3. For all PCB candidates, confirm the presence of an (M-70) – ion cluster by examining ICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.

12.4.4. For Cl_3 -Cl_7 isomer groups, examine ICPs or spectra for intense (M+70) + ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data show that this is not a potential problem for other PCB isomer groups.) If this interference occurs, a correction can be produced. Obtain and record the area for the appropriate ion (Table 7) for the candidate PCB isomer group. Use the information in Table 8 to correct the measured abundance of M+. For example, if a Cl_7 -PCB and a Cl_5 -PCB candidate coelute, the Cl_7 -PCB will contribute to the ion measured for m/z 326 and m/z 324, the quantitation and confirmation ions, respectively, for a Cl_5 -PCB. Obtain and record the area for m/z 322 (the lowest mass ion in the (M+-70) + ion cluster of a Cl_5 -PCB fragment produced by a Cl_7 -PCB). To determine the m/z 326 and m/z 324 areas produced by the Cl_5 -PCB, calculate the Cl_7 -PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for m/z 322 should be subtracted from the area measured for m/z 324, and 108% of the m/z 322 area should be subtracted from the area measured for m/z 326 (Table 8).

12.4.5. For Cl_2 –Cl_8 -PCB candidates, examine ICPs or spectra for intense (M+35) + ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because of the natural abundance of ^{13}C. (This interference will be small and can be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of another PCB containing one more chlorine). To correct for this interference, obtain and record the area for the appropriate ion (Table 9) from the (M-1) + ion cluster, and subtract 13.5% of the area measured for the (M-1) + ion from the measured area of the quantitation ion. For example, for Cl_5 -PCB candidates, obtain and record the area for m/z 325; subtract 13.5% of that area from the measured area of m/z 326.

12.4.6. Use ICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 7). If acceptable ratios are not obtained, a coeluting or closely eluting compound may be interfering. Examination of data from several scans may

provide information that will allow application of additional background corrections to improve the ion ratio.

12.5. **Identification Criteria:**

12.5.1. Chrysene-d12: the abundance of m/z 241 relative to m/z 240 must be ≥ 15% and ≤ 25%, and these ions must maximize simultaneously. The area measured for m/z 240 must be within 30% of the area measured during the most recent calibration.

12.5.2. Phenanthrene-d10: the abundance of m/z 189 relative to m/z 188 must be ≥ 10% and ≤ 22%, and these ions must maximize simultaneously. The area measured for m/z 188 must be within 30% of the area measured during the most recent calibration.

12.5.3. Internal standard and surrogate retention times must be within ±10 s of that observed during the last previous continuing calibration check.

12.5.4. Quantitation and confirmation ions for each PCB isomer group must maximize within ±1 scan of each other.

12.5.5. The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

12.5.6. For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown on Table 7; at least one ion in the (M-70) + ion cluster most be present.

13. Quality Control

13.1. Before processing any samples the analyst must demonstrate that interference from the analytical system and glassware are under control. Each time a batch of $\leq$20 samples is extracted or reagents are changed a method blank must be processed as a safe guard against laboratory contamination. A method blank contains the same amount of surrogate compounds and internal standards that is added to each sample.

13.2. Before a new batch of solvents or reagents is used for sample extraction of for column chromatographic procedures, analyze a method blank. In addition, analyze a laboratory solvent blank (LSB), which is the same as an method blank except that no surrogate or internal standard compounds are added. This demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quanitation ions for those compounds.

13.3. An acceptable method blank contains no method analyte at a concentration greater than its reporting limit (RL) for the PCB homologue and contains no additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte at its RL. If the method blank that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reanalyzed, if possible.

13.4. Surrogate recoveries must be calculated for each sample and associated quality control samples. If any surrogate in the blank or LCS is not within acceptance limits, all samples for that batch must be re-extracted and re-analyzed. If a surrogate falls outside of QC limits for a particular sample the sample should be checked for matrix effects and re-extracted or re-analyzed as necessary.

13.4.1. Water, Soil, Sediment Samples: Surrogate recoveries for both TCMX and D[$^{13}C_{12}$]BP should be within 60-140 %.

13.4.2. TO-10A PUF Samples: TCMX recovery should be within 42.5-134% and D[$^{13}C_{12}$]BP within 70.1-116%.

13.4.3. TO-4A PUF Samples: TCMX recovery should be within 17.9-137% and D[$^{13}C_{12}$]BP within 44.4-104%.

13.5. In this method, the 680 spike standard is used as the laboratory performance check solution (LCS). Calculate the percent recovery for the spike and compare to the limits of 60-140%. If the percent recovery for the (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be reanalyzed if possible. (Exception: If the LCS recovery is high and there were no associated positive results, then address the issue in the Case Narrative and no further action is needed).

13.5.1. Waters: Add 250µL of 680 spike standard (5mL final volume).

13.5.2. Solids: Add 2500µL of 680 spike standard (25mL final volume).

13.5.3. PUF: Add 100µL of 680 spike standard (1.0mL final volume).

13.6. One set of Matrix Spike (MS or M), Matrix Spike Duplicate (MSD or K) should be extracted with each group of 20 samples (spiked the same as the LCS above). Recoveries are compared to laboratory generated control limits. If compounds are outside of recovery limits in the matrix spike but the LCS meets the criteria the system is in control and reanalysis of the MS and MSD is not required. If any compound is outside of the recovery limits for the LCS all samples and QC must be re-extracted and reanalyzed.

13.7. Calculate the percent recovery based on Aroclor concentration of both samples as follows:

Percent Recovery (p) = 100 (A-B) %/T

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike

13.8. Compare the percent recovery calculated with the project limits of 60-140%. If the total PCB concentrations of the matrix spikes are *greater* than four times the calculated sample amount, then the quality control limits should be applied. If the total PCB concentrations of the matrix spikes are ***less*** than four times the sample, then there are no established limits applicable. If the percent recovery falls outside of the acceptance range for the total PCB used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Check for documentable errors (e.g., calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated LCS is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

13.9. A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

RPD = [(A-B)/{(A+B)/2}] x 100

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample
where (A-B) is taken as an absolute value

13.10. If the total PCB concentrations of the matrix spike set are *greater* than four times the calculated sample amount, then an RPD of 40% or less is acceptable. If the total PCB concentrations of the matrix spike set is

less than four times the calculated sample amount than there are no established limits applicable to the RPD. If the criterion is not met, check for documentable errors (e.g., calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated LCS is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

14. Data Analysis and Calculations

14.1. Calculations for DFTPP are handled through the Target™ processing software. All other calculations for calibration and sample analysis are handled through the automated ion extraction and measurement software.

14.2. From appropriate ICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.

14.3. Any individual PCB analyte amount in a sample or QC sample above the initial low-level calibration standard concentration will be reported as such with no associated flags. Any individual PCB analyte amount that exceeds the high level calibration standard of the calibration curve will require dilution and re-analysis of the extract to place that analyte within the calibration range.

14.4. A Method Detection Limit (MDL) will be performed in accordance with procedures set forth in 40CFR Part 136, Appendix B. Any individual PCB analyte amount in a sample or QC sample that is above the established MDL but below the initial low level calibration standard concentration will be reported and appropriately flagged with a "J" flag. A "J" flag signifies that the analyte amount was below the initial low level calibration standard concentration but above the determined MDL for the analyte.

14.5. Any individual PCB analyte amount in a sample or QC sample that is below the established MDL for that analyte or not present will be reported as not detected (ND). The associated MDL concentration value for that analyte will be reported to provide information on the analyte reporting limit.

14.6. For each PCB homolog group all reportable (both non-flagged and "J" flagged) PCB analytes associated with a given chlorination level (i.e., All dichlorobiphenyls) will be summed and a total provided. No flagging of homolog group concentrations will occur. This will provide 10 PCB sub-totals from monochlorobiphenyl to decachlorobiphenyl. If for a given homolog there are no reportable analytes to report or sum, then a not detected (ND) will be reported. The associated analyte MDL concentration value for that chlorination level will be reported as the homolog reporting limit.

14.7. The total PCB amount for a sample or QC sample will be provided by summation of the homolog group amounts. No flagging of the total PCB amount will occur. If all 10 homolog groups are reported as not detected (ND), then the total PCB amount will be reported as not detected (ND). For this reporting condition (i.e., total PCB amount = ND), the single highest reporting limit from the 10 homolog groups (highest PCB analyte MDL from MDL study) will be used and will provide the reporting limit for the Total PCB amount.

14.8. All solid sample results will be reported on a dry-weight basis.

14.9. For PCBs, sum the areas for all isomers identified at each level of chlorination (e.g., sum all quantitation ion areas for Cl_4 -PCBs).

14.10. For the initial calibration use the average calculated RF. **Caution: For PCB analysis with automated data interpretation a linear fit algorithm will produce erroneous concentration data.**

14.11. Use the RF relative to chrysene-d12 unless an interference makes the use of the RF relative to phenanthrene-d10 necessary.

14.12. Report calculated values to two significant figures.

14.13. When samples of known composition or fortified samples are analyzed, calculate the percent method bias using the equation:

$$B = 100 (C_s - C_t)/ C_t$$

C_s = measured concentration (in µg/Kg or µg/L) and
C_t = theoretical concentration (i.e., the quantity added to the sample aliquot/weight or volume of sample aliquot).
Note: The bias value retains a positive or negative sign.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Data is assessed based on ion intensity, relative retention time and analyst knowledge.

15.2. A method blank is analyzed with each analytical batch.

15.3. Internal standard responses must be within 30% from the area measured in the most recent previous analysis of a calibration solution or within 50% from the mean area measured during initial calibration.

15.4. Measure the concentration of both surrogate compounds in every sample and blank. Acceptance limits for surrogate compounds is 60-140%.

15.5. A Laboratory Control Sample (LCS) is also prepared and analyzed with each batch. Acceptance limits for surrogate compounds is 60-140%. If the percent recovery for the (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be reanalyzed if possible. (Exception: If the LCS recovery is high and there were no associated positive results, then address the issue in the Case Narrative and no further action is needed).

16. Corrective Actions for Out-of-Control Data

16.1. If a method blank is not within acceptance limits, the system is checked for the source of blank contamination and no samples are analyzed until a satisfactory blank is achieved.

16.2. If a LCS is not within acceptance criteria, no data is accepted from that batch and the problem is located and corrected to produce acceptable results.

16.3. If the internal standard response fails acceptance criteria, the problem is located and the sample is either re-analyzed immediately or, a new initial calibration curve is analyzed and the sample is then re-analyzed. If sample results are accepted or the samples cannot be re-analyzed, they will be qualified on the analytical report.

16.4. If a surrogate is not within acceptance limits, it is normally due to matrix interference. Failed surrogate recoveries are reported to the client on the analytical report. If a systematic failure is occurring the problem is located and corrected.

16.5. MS/MSD pair failures are reported to the client, but if the LCS meets criteria the sample batch data is reported.

16.6. See the QA Plan for corrective actions for policies, procedures and quality control for further corrective action.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Data that is out-of-control is either re-analyzed or, if that is not possible, commented to the client on the analytical report. The analytical system is then inspected to determine why the data was unacceptable and corrective action is taken to remedy the situation.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. Initial Demonstration of Capability (IDOC):

18.2.1. Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory maintains records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

18.3. Demonstration of Capability (DOC):

18.3.1. Each analyst must make an initial, one-time, demonstration of the ability to generate acceptable precision and accuracy with this method, known as the initial demonstration of capability (IDOC). A continuing demonstration of capability (CDOC) is required annually.

18.3.2. Waters: Prepare a QC check sample by adding 100µL of the 680 spike standard and 200 µL of the TCMX Surrogate at 0.50µg/mL to each of four (4) aliquots of reagent water samples. Extract samples according to SOP S-NY-O-141 and analyze extracts as described in the procedure section. Calculate the average recovery and the standard deviation in µg/L.

18.3.3. Solids: Prepare a QC check sample by adding 500µL of the the 680 spike standard and 1000µL of the TCMX Surrogate at 0.50µg/mL to each of four (4) solid samples. Extract samples according to SOP S-NY-O-323 and analyze extracts as described in the procedure section. Calculate the average recovery and the standard deviation in µg/kg.

18.3.4. PUF: Prepare a QC check sample by adding 100µL of the the 680 spike standard and 100µL of the TCMX Surrogate at 0.20µg/mL to each of four (4) PUFs. Extract samples according to SOP S-NY-O-151 and S-NY-O-241 and analyze extracts as described in the procedure section. Calculate the average recovery and the standard deviation in µg/PUF.

18.4. Method Detection Limits:

18.4.1. A method detection limit will be determined for this method, as described in 40 CFR 136 Appendix B, whenever a major modification to the preparation or analysis procedures is made. See SOP S-NY-Q-021 current revision for further details.

18.4.2. Waters: Using a syringe, prepare the MDL samples by adding 10.0µL of the 680 spike standard and 200µL of the TCMX Surrogate at 0.5µg/mL to each of eight (8) aliquots of reagent water samples. Extract samples according to SOP S-NY-O-141 and analyze extracts as described in the procedure section.

18.4.3. Solids: Using a syringe, prepare the MDL samples by adding 50.0µL of the 680 spike standard and 1000 µL of the TCMX Surrogate at 0.5µg/mL to each of eight (8) solid samples. Extract samples according to SOP S-NY-O-323 and analyze extracts as described in the procedure section.

18.4.4. PUFs: Using a syringe, prepare the MDL samples by adding 20.0µL of the 680 spike standard and 500µL of the TCMX Surrogate at 0.2µg/mL to each of eight (8) PUFs. Extract samples according to SOP S-NY-O-151 and SOP S-NY-O-241 and analyze extracts as described in the procedure section.

19. Method Modifications

19.1. The laboratory also analyzes TO-10A and TO-4A polyurethane foam (PUF) cartridges using this method. EPA Method 680 does not designate polyurethane foam as an applicable matrix.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Calibration, surrogate, and internal standards are all possible carcinogens. Prepare all standards. Complete all spiking and prepare all dilutions in a hood.

22.2. Safety glasses, lab coat, and gloves are required.

22.3. Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the project laboratory's internal chemical hygiene plan for further safety information.

23. Waste Management

23.1. All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

23.2. Please refer to SOP S-NY-W-054 regarding how hazardous waste is handled and disposed of by the laboratory.

24. Pollution Prevention

24.1. Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures.

24.2. Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP S-NY-S-168.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. Glaser, J. A., D. L. Foerst, G. D. McKee, S. A. Quave, and W. L. Budde, "Trace Analyses for Wastewaters", Environ. Sci. Technol. 15, 1426, 1981.

25.5. Ballschmiter, K. and M. Zell, Fresenius Z. Anal. Chem., 302, 20, 1980.

25.6. "Carcinogens -- Working with Carcinogens", Department of Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

25.7. "OSHA Safety and Health Standards, General Industry", 29 CPR 1910, Occupational Safety and Health Administration, OSHA 2206, Revised January 1976.

25.8. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication Committee on Chemical Safety, 3rd Edition, 1979.

25.9. Gebhart, J. E., Hayes, T. L., Alford-Stevens, A. L., and W. L. Budde, "Mass Spectrometric Determination of Polychlorinated Biphenyls as Isomer Groups", Anal. Chem. 57, 2458, 1985.

25.10. Rote, J. W. and W. J. Morris, "Use of Isotopic Abundance Ratios in Identification of Polychlorinated Biphenyls by Mass Spectrometry", J. Assoc. Offic. Anal. Chem. 56 (l), 188, 1973.

25.11. EPA Method 680 –EMSL Cincinnati, Ohio: Ann Alford-Stevens, Thomas A. Bellar, James W. Eichelberger, William L. Budde. November 1985.

25.12. Target™ Software, Thru-put Systems, Inc., Orlando Fl 32819.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Table 1: DFTPP Ion Abundance Criteria.

26.2. Table 2: DFTPP Temperature Program.

26.3. Table 3: Method Temperature Program.

26.4. Table 4: PCB Congeners Used as Calibration Standards.

26.5. Table 5: Curve Preparation.

26.6. Table 6: Composition and Concentrations of SIM Calibration Solutions.

26.7. Table 7: Quantitation Confirmation, and Interference Check Ions for PCBs, Internal Standards and Surrogate Compounds.

26.8. Table 8: Correction for Interference of PCB Containing Two Additional Chlorines.

26.9. Table 9: Correction for Interference of PCB Containing One Additional Chlorine.

26.10. Table 10: Known Relative Abundances of Ions in PCB Molecular Ion Clusters.

26.11. Table 11: Retention Time Data for PCB Isomer Groups and Calibration Congeners.

26.12. Table 12: Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions.

26.13. Table 13: Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤ 27 Ions.

26.14. Figure 1: Merged Ion Current Profile of PCB Calibration Congeners.

26.15. Figure 2: Total Ion Chromatogram of PCB Window Defining Mixture Standard.

27. Revisions

Document Number	Reason for Change	Date
S-NY-O-040-rev.07	General: converted to new format. Sections 25.1-25.3: added standard Pace references.	09Jan2015
S-NY-O-040-rev.08	General: Added information for analysis of polyurethane foam (PUF) matrix and updated SOP references. Sections 8.12 and 13.2: added requirement for a laboratory solvent blank Section 10.6.2: added recipe for preparation of DCBP surrogate at 1.0ug/mL concentration Sections 13.5, 18.3.2, and 18.3.3: updated spike mix used Section 19.1: added analysis of PUF matrix as a method modification	02July2015

Table 1: DFTPP Ion Abundance Criteria

MASS	m/z ABUNDANCE CRITERIA
127	40-60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100% relative abundance
199	5-9 percent of mass 198
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

Table 2: DFTPP Temperature Program

Column

Temperature (ºC)	Ramp (ºC/min)	Hold time (min)	Final Time (min)
50	0.00	2.00	2.00
160	30	1.00	6.67
202	3.00	0.00	20.67
260	50	0.00	21.83

Injector

Temperature (ºC)	Ramp (ºC/min)	Hold time (min)	Final Time (min)
62	0.00	0.30	0.30
250	150	20.28	21.83

Table 3: Method Temperature Program

Column

Temperature (ºC)	Ramp (ºC/min)	Hold time (min)	Final Time (min)
50	0.00	2.00	2.00
160	30	1.00	6.63
280	3.00	0.00	46.67

Injector

Temperature (ºC)	Ramp (ºC/min)	Hold time (min)	Final Time (min)
62	0.00	0.30	0.30
275	150	44.95	46.67

Table 4: PCB Congeners Used as Calibration Standards

PCB Isomer Group	Congener Number[a]	Chlorine Substitution
Concentration Calibration Standard		
Monochlorobiphenyl	1	2
Dichlorobiphenyl	5	2, 3
Trichlorobiphenyl	29	2, 4, 5
Tetrachlorobiphenyl	50	2, 2', 4, 6
Pentachlorobiphenyl	87	2, 2', 3, 4, 5
Hexachlororbiphenyl	154	2, 2', 4, 4', 5, 6'
Heptachlorobiphenyl	188	2, 2', 3, 4', 5, 6, 6'
Octachlorobiphenyl	200	2, 2', 3, 3', 4, 5', 6, 6'
Nonachlorobiphenyl[b]	----	----
Decachlorobiphenyl	209	2, 2', 3, 3', 4, 4', 5, 5', 6, 6'
Retention Time Calibration Standard		
Tetrachlorobiphenyl	77	3, 3', 4, 4'
Pentachlorobiphenyl	104	2, 2', 4, 6, 6'
Heptachlorobiphenyl	189	2, 3, 3', 4, 4', 5, 5'
Octachlorobiphenyl	202	2, 2', 3, 3', 5, 5', 6, 6'

[a] Numbered according to the system of Ballschmiter and Zell (2).

[b] Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl isomer groups

Table 5: Curve Preparation

Calibration Level	680 Stock STD Volume (µL)	D[$^{13}C_{12}$]BP Volume (µL)	n-Hexane Volume (µL)	Final Volume (µL)
7	1000	0	0	1000
6	600	300	100	1000
5	400	200	400	1000
4	200	100	700	1000
3	100	50	850	1000
2	10	5.0	985	1000
1	2.0	1.0	997	1000

Table 6: Composition and Concentrations of SIM Calibration Solutions

Concentration (ng/mL)							
Compound (Congener)	**CAL 1**	**CAL 2**	**CAL 3**	**CAL 4**	**CAL 5**	**CAL 6**	**CAL 7**
Cl_1 (#1)	0.01	0.05	0.5	1.0	2.0	3.0	5.0
Cl_2 (#5)	0.01	0.05	0.5	1.0	2.0	3.0	5.0
Cl_3 (#29)	0.01	0.05	0.5	1.0	2.0	3.0	5.0
Cl_4 (#50)	0.02	0.10	1.0	2.0	4.0	6.0	10
Cl_5 (#87)	0.02	0.10	1.0	2.0	4.0	6.0	10
Cl_6 (#154)	0.02	0.10	1.0	2.0	4.0	6.0	10
Cl_7 (#188)	0.03	0.15	1.5	3.0	6.0	9.0	15
Cl_8 (#200)	0.03	0.15	1.5	3.0	6.0	9.0	15
Cl_{10} (#209)	0.05	0.25	2.5	5.0	10	15	25
RT Congeners							
Cl_4 (#77)	0.02	0.10	1.0	2.0	4.0	6.0	10
Cl_5 (#104)	0.02	0.10	1.0	2.0	4.0	6.0	10
Cl_9 (#208)	0.04	0.20	2.0	4.0	8.0	12	20
Internal Standards							
Chrysene-d12	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Phenanthrene-d10	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Surrogate Compounds							
TCMX	0.01	0.05	0.5	1.0	2.0	3.0	5.0
D[$^{13}C_{12}$]BP	0.05	0.25	2.5	5.0	10	15	----

Table 7: Quantitation Confirmation, and Interference Check Ions for PCBs, Internal Standards and Surrogate Compounds

Analyte	Nom MW	Quant Ion	Confirm Ion	Expected Ratio[a]	Accept Ratio[a]	M –70 Confirm Ion	Interference Check Ions M +70	M +35
PCB Isomer Group								
Cl_1	188	188	190	3.0	2.5 – 3.5	152[b]	256	222
Cl_2	222	222	224	1.5	1.3 – 1.7	152	292	256
Cl_3	256	256	258	1.0	0.8 – 1.2	186	326	290
Cl_4	290	292	290	1.3	1.1 – 1.5	220	360	326
Cl_5	324	326	324	1.6	1.4 – 1.8	254	394	360
Cl_6	358	360	362	1.2	1.0 – 1.4	288	430	394
Cl_7	392	394	396	1.0	0.8 – 1.2	322	464	430
Cl_8	426	430	428	1.1	0.9 – 1.3	356	498	464
Cl_9	460	464	466	1.3	1.1 – 1.5	390	--	498
Cl_{10}	494	498	500	1.1	0.9 – 1.3	424	--	--
Internal Standards								
Chrysene-d12	240	240	241	5.1	4.3 – 5.9	--	--	--
Phenanthrene-d10	188	188	189	6.6	6.0 – 7.2	--	--	--
Surrogate Compounds								
TCMX	244	242	244	1.3	1.1 – 1.5	--	--	--
D[$^{13}C_{12}$]BP	510	510	512	1.1	0.9 – 1.3	--	--	--

[a] Ratio of quantitation ion to confirmation ion.
[b] Monochlorobiphenyls loses HCl to produce an ion at m/z 152.

Table 8: Correction for Interference of PCB Containing Two Additional Chlorines

Candidate Isomer Group	Quant. Ion	Confirm. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from	
				Quant. Ion Area	Confirm Ion Area
Trichlorobiphenyls	256	258	254	99	33
Tetrachlorobiphenyl	292	290	288	61	131
Pentachlorobiphenyls	326	324	322	108	164
Hexachlorobiphenyls	360	362	356	161	71
Heptachlorobiphenyls	394	396	390	225	123

Table 9: Correction for Interference of PCB Containing One Additional Chlorine

Candidate Isomer Group	Quant. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant. Ion Area
Dichlorobiphenyls	222	221	13.5
Trichlorobiphenyls	256	255	13.5
Tetrachlorobiphenyl	292	289	17.4
Pentachlorobiphenyls	326	323	22.0
Hexachlorobiphenyls	360	357	26.5
Heptachlorobiphenyls	394	391	30.9
Octachlorobiphenyls	430	425	40.0

Table 10: Known Relative Abundances of Ions in PCB Molecular Ion Clusters

mz	Relative Intensity	mz	Relative Intensity	mz	Relative Intensity	mz	Relative Intensity
Monochlorobiphenyls		**Pentachlorobiphenyls**		**Heptachlorobiphenyls**		**Nonachlorobiphenyls**	
188	100	324	61.00	392	43.70	460	26.00
189	13.50	325	8.26	393	5.91	461	3.51
190	33.40	326	100	394	100	462	76.40
192	4.41	327	13.50	395	13.50	463	10.30
		328	65.70	396	98.30	464	100
Dichlorobiphenyls		329	8.78	397	13.20	465	13.40
222	100	330	21.70	398	53.80	466	76.40
223	13.50	331	2.86	399	7.16	467	10.20
224	66.00	332	3.62	400	17.70	468	37.60
225	8.82	333	0.47	401	2.34	469	5.00
226	11.20	334	0.25	402	3.52	470	12.40
227	1.44			403	0.46	471	1.63
		Hexachlorobiphenyls		404	0.40	472	2.72
Trichlorobiphenyls		358	50.90			473	0.35
256	100	359	6.89	**Octachlorobiphenyls**		474	0.39
257	13.50	360	100	426	33.40		
258	98.60	361	13.50	427	4.51	**Decachlorobiphenyls**	
229	13.20	362	82.00	428	87.30	494	20.80
260	32.70	363	11.00	429	11.80	495	2.81
261	4.31	364	36.00	430	100	496	68.00
262	3.73	365	4.77	431	13.40	497	9.17
263	0.47	366	8.92	432	65.60	498	100
		367	1.17	433	8.76	499	13.40
Tetrachlorobiphenyls		368	1.20	434	26.90	500	87.30
290	76.20	369	0.15	435	3.57	501	11.70
291	10.30			436	7.10	502	50.00
292	100			437	0.93	503	6.67
293	13.40			438	1.18	504	19.70
294	49.40			439	0.15	505	2.61
295	6.57			440	0.11	506	5.40
296	11.00					507	0.71
297	1.43					508	1.02
298	0.95					509	0.13

[a] Source: Rote and Morris (7)

Table 11: Retention Time Data for PCB Isomer Groups and Calibration Congeners

Isomer Group	Approx. RRT Range[a]	Cal. Congener Number	Cal. Congener RRT[a]
Monochlorobiphenyls	0.27-0.32	1	0.27
Dichlorobiphenyls	0.33-0.47	5	0.38
Trichlorobiphenyls	0.41-0.63	29	0.49
Tetrachlorobiphenyl	0.48-0.79	50	0.50
Pentachlorobiphenyls	0.58-0.94	87	0.75
Hexachlorobiphenyls	0.68-1.07	154	0.76
Heptachlorobiphenyls	0.82-1.12	188	0.82
Octachlorobiphenyls	0.96-1.17	200	0.98
Nonachlorobiphenyls	1.11-1.21	--	--
Decachlorobiphenyls	1.25	209	1.25

[a] Retention time relative to Chrysene-d12 with a 30m × 0.25mm ID DB-XLB fused silica capillary column and the GC conditions set forth in Table 3

Table 12: Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions

Ion Set #1[a]	Ion Set #2[b]	Ion Set #3[c]	Ion Set #4[d]	Ion Set #5[e]
152	186	247	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
242	292	357	362	432
244	294	358	390	462
255	323	360	391	464
256	324	362	392	466
258	326	392	394	496
290	328	394	396	498
292	358	396	398	499
294	360	398	425	500
	362		426	502
			428	510
			430	512
			432	
			460	
			462	
			464	
			466	
19 ions	**20 ions**	**19 ions**	**27 ions**	**22 ions**

[a] Ions to identify and measure Cl_1 – Cl_4 PCBs, TCMX and phenanthrene-d10.
[b] Ions to identify and measure Cl_3– Cl_6 PCBs.
[c] Ions to identify and measure Cl_5 – Cl_7 PCBs.
[d] Ions to identify and measure Cl_6 – Cl_9 PCBs and chrysene-d12.

[e] Ions to identify and measure $Cl_8 - Cl_{10}$ PCBs and D[$^{13}C_{12}$]BP.

Table 13: Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions

Ion Set	Isomer Group/ IS/Surrogate	Quant. Ion	Confirm. Ion	M –70 Ions	M +70 Ions	M +35 Ions	Ion Measured[a] For Correction
1	Cl_1	188	190	152, 153[b]	256, 258	222, 224	-- --
	Cl_2	222	224	152, 153, 186, 188[c]	290, 292, 294	256, 258	-- 221
	Cl_3	256	258	186, 188	--	290, 292, 294	-- 255
	Cl_4	292	290, 294	220, 222	--	--	-- --
	TCMX	244	242	--	--	--	-- --
	Phenanthrene-d10	188	189	--	--	--	-- --
2	Cl_3	256	258	186, 188	324, 326, 328	290, 292, 294	254 255
	Cl_4	292	290, 294	220, 222	360, 362	324, 326, 328	288 289
	Cl_5	326	324, 328	254, 256, 258	--	360, 362	-- 323
	Cl_6	360	358, 362	288, 290, 292	--	--	-- --
3	Cl_5	326	324, 328	254, 256	392, 394, 396, 398	360, 362	322 323
	Cl_6	360	358, 362	288, 290	--	392, 394, 396, 398	-- 357
	Cl_7	394	396, 398	322, 324, 326	--	--	-- --
4	Cl_6	360	358, 362	288, 290	426, 428, 430, 432	392, 394, 396	356 357
	Cl_7	394	396, 398	322, 324	--	428, 430, 432	-- 391
	Cl_8	430	428, 432	356, 358, 360	--	--	-- --
	Chrysene-d12	240	241	--	--	--	-- --
5	Cl_8	430	428, 432	356, 358, 360	494, 496, 498, 500	462, 464, 466	-- 425
	Cl_9	464	462, 466	390, 392, 394	--	496, 498, 500	-- --
	Cl_{10}	498	496, 500	424, 426, 428, 430	--	--	-- --

	D[$^{13}C_{12}$]BP	510	512	--	--	--	--	--

[a] See Tables 7-8.
[b] Cl_1 PCBs lose HCl.
[c] Some Cl_2 PCBs lose Cl_2 and some lose HCl.

Figure 1: Merged Ion Current Profile of PCB Calibration Congeners

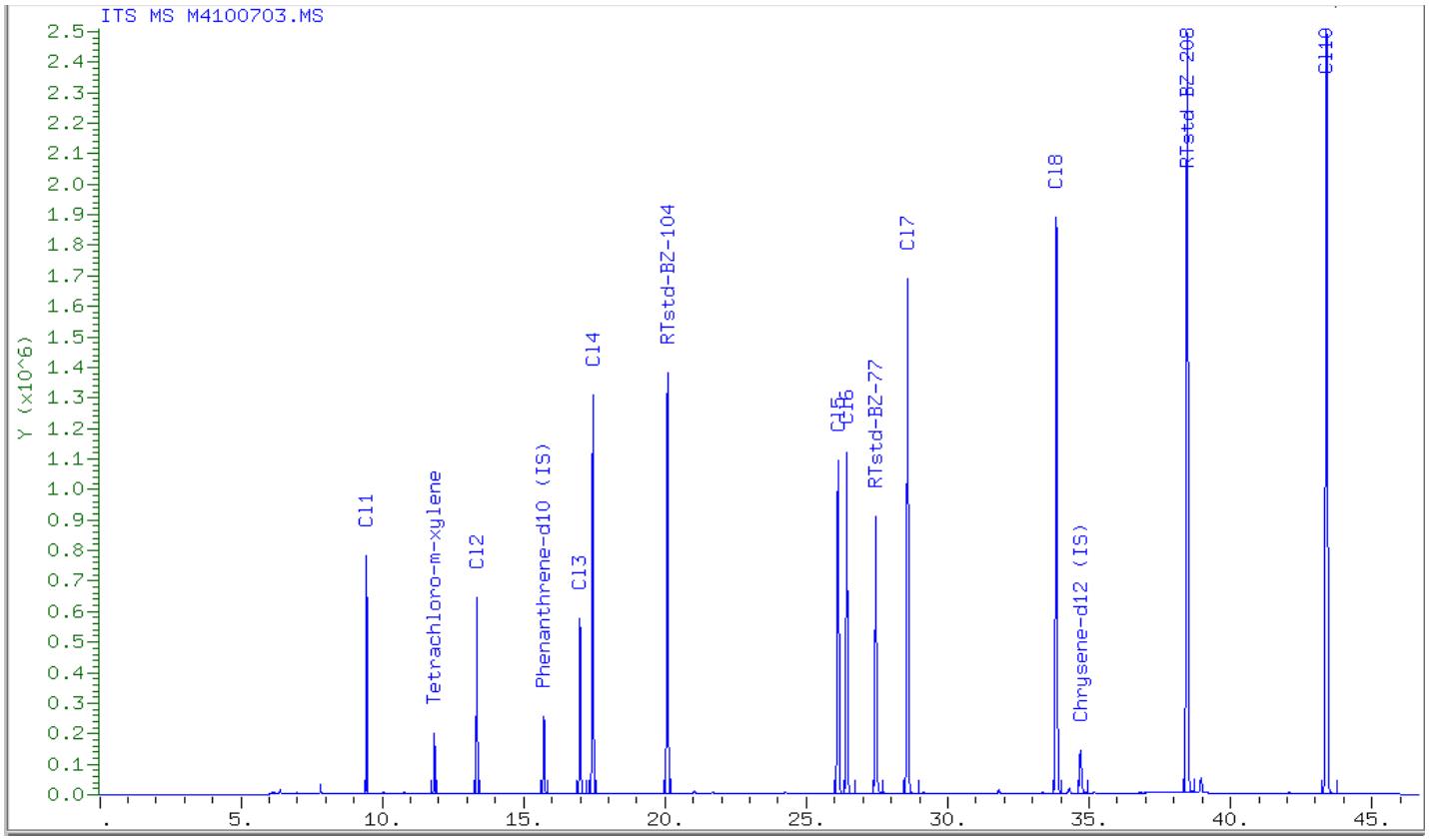
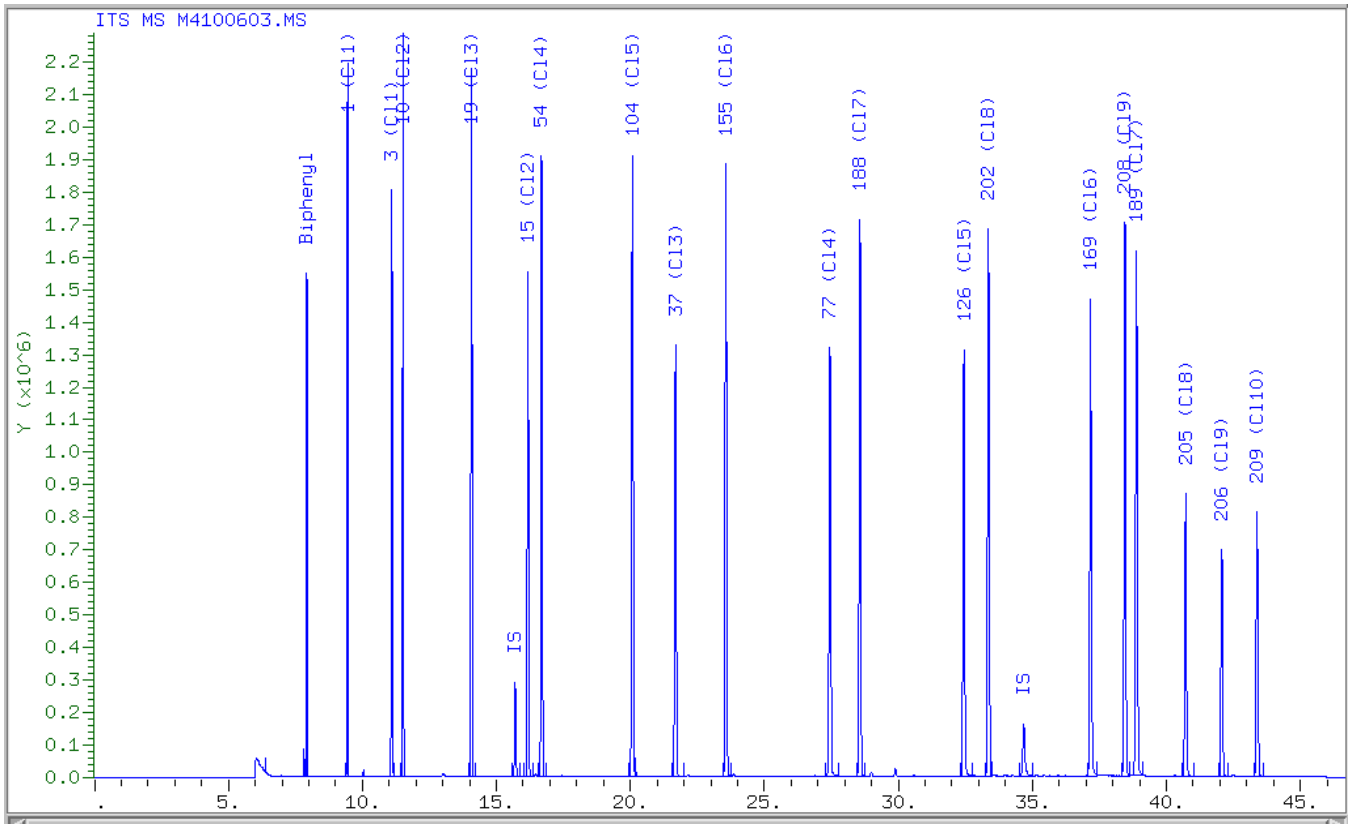


Figure 2: Total Ion Chromatogram of PCB Window Defining Mixture Standard



STANDARD OPERATING PROCEDURE

Preparation of Aqueous Samples for ICP Analysis

Method 3005A

SOP NUMBER:	PGH-M-015-8
REVIEW:	C. Steinbach and B Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-M-015-7
REVIEW DATE:	Upon Procedural Change

APPROVALS

Marla L. Kruth

Assistant General Manager — 06/27/14 Date

Maureen K. DeRubeis

Senior Quality Manager — 07/15/14 Date

Department Manager/Supervisor — 07/15/14 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

1. Purpose

1.1 This SOP documents the procedure to be followed for the preparation of aqueous samples for Inductively Coupled Plasma (ICP) Analysis.

2. Scope and Application

2.1 This SOP provides the sample preparation procedures for the determination of total, dissolved and recoverable analytes in groundwater, surface waters and wastewaters for analysis by ICP-AES.

2.2 Samples that are to be analyzed for dissolved metals need to be filtered at the time of collection or prior to acidification with nitric acid.

2.3 Samples prepared by this method may be analyzed by ICP for the following metals:

Aluminum	Magnesium
Antimony	Manganese
Arsenic	Molybdenum
Barium	Nickel
Beryllium	Potassium
Boron	Selenium
Cadmium	Silicon (as S_1O_2)
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

3. Summary of Method

3.1 50mL of a well mixed, acidified, aqueous sample is poured into a polypropylene digestion vessel. Acid is then added to the digestion vessel and the sample are placed in a hotblock digester and heated to 95±2°C, which will substantially reduce the volume. The sample is then cooled, and diluted back up to volume with reagent water and submitted for analysis.

3.1.1 For dissolved metals, the aqueous sample must be filtered through a 0.45µm filter and acidified with 1:1 nitric acid to a pH<2.

4. Interferences

4.1 Some metal complexes may be destroyed if the samples are digested to vigorously.

4.2 Precipitation of the sample may cause low silver concentrations, resulting in inaccurate results.

5. Safety

5.1 Analysts should take necessary safety precautions when handling chemicals and samples. The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation.

5.2 Proper personal protection equipment must include, at a minimum, a lab coat, gloves, and safety glasses.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye protection, gloves, and lab coat must be worn.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be performed in a fume hood.

5.5 Analysts should be familiar with the SDS sheets for all chemicals and reagents used in this procedure and the location of the SDS sheets within the laboratory.

5.6 For any accidental spills or contact with the reagents, refer to the corresponding SDS..

5.7 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.8 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.9 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 Calibration Blank - A volume of reagent water acidified with the same acid matrix used in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument. In this procedure, the calibration blank is equivalent to an instrument blank.

6.3 Continuous Calibration Verification (CCV) - A solution of the method analyte, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

6.4 Initial Calibration Verification (ICV) - A solution of the method analyte of known concentration which is used to fortify an LCS or MS. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards.

6.5 Batch- A set of no more than 20 samples, each of which is a well mixed aliquot of an aqueous solution. In addition to the samples, a method blank, an LCS, an MS/MSD pair and two duplicate samples are included in the batch.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

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7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to withdrawing an aliquot for processing (direct analysis) to ensure that the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

8.1.1 Do not dip pH paper or a pH meter directly into the sample; remove a small aliquot and test the aliquot. Discard the aliquot of sample after the pH measurement has been performed.

8.2 For the determination of the dissolved elements, an unpreserved portion of the sample must be filtered through a 0.45μm membrane filter at the time of collection or as soon thereafter as practically possible. (A glass or plastic filtering apparatus is recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silicon are critical). Use a portion of the filtered sample to rinse the filter flask; discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 HNO_3 to a pH<2 immediately following filtration.

8.3 Samples are not filtered for the determination of total recoverable elements in aqueous samples, but are acidified with 1:1 HNO_3 to a pH<2.

8.3.1 Normally, 3mL of 1:1 acid per liter of sample is sufficient for most ambient water samples.

8.3.2 Preservation may be performed at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, it is recommended that samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory.

8.3.3 Following acidification, the sample should be mixed, held for 24 hours, and then verified to be pH <2 just prior to withdrawing an aliquot for processing (direct analysis).

8.3.3.1 If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added, and the sample held for 24 hours until verified to be pH <2.

After the sample is verified to be pH <2, make a note of it in the comment section of the prep logbook that the pH <2.

8.3.4 When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

8.3.5 A dissolved Method Blank (MB) and Laboratory Control System (LCS) must be placed through the same process as the dissolved samples.

8.4 A field blank should be prepared and analyzed if required by the sample submitter. Use the same conditions (i.e., container, filtration and preservation) used in sample collection.

9. Equipment and Supplies

9.1 Environmental Express® Hotblock or a temperature adjustable hotplate (or equivalent).

9.2 Disposable polypropylene digestion vessels (PDV) with caps, or 250mL glass beakers with ribbed watch glasses.

9.3 Environmental Express® Hotblock Rack (or equivalent).

9.4 Thermometer- Traceable to NIST Calibration and capable of measuring. 90-95°C.

9.5 Fisherbrand® Filters- 0.45µm membrane mixed cellulose ester (MCE) 47mm non-sterile (or equivalent).

9.6 Nalgene® Side Arm Flask.

9.7 Magnetic Filter Funnel.

9.8 Class A and Air Displacement Calibrated Pipettes, Glass.

9.9 Class A Volumetric Flasks and Graduated Cylinders, Glass.

9.10 Nalgene® Wash bottle.

9.11 Sample bottles with lids.

9.12 Flipmate filters and 100mL PDVs (or equivalent).

10. Reagents and Standards

10.1 Record all the identifications for all standards and solutions that will be used in the metals standard logbook. (See attachment No.1).

10.2 Reagent (Millipore Type II) Water (DI Water).

10.3 Nitric Acid(HNO_3)- SCP Science PlasmaPure (or equivalent).

10.4 Hydrochloric Acid(HCl)- SCP Science PlasmaPure (or equivalent).

10.5 Inorganic Ventures PA-Standard 1B (or equivalent). See the Certificate of Analysis and/or Standard logbook for concentrations.

10.6 Inorganic Ventures PA-Standard 2B (or equivalent). See the Certificate of Analysis and/or Standard logbook for concentrations.

10.7 Inorganic Ventures PA-Standard 3B (or equivalent). See the Certificate of Analysis and/or Standard logbook for concentrations.

10.8 For relevant information, such as purification, storage conditions, and expiration dates for standards, chemicals, and reagents refer to the Certificate of Analysis located in the preparation area.

11. Calibration

11.1 The temperature of the hotblock will be calibrated against a thermometer that is NIST traceable to verify the temperature of the solution in the PDV.

11.1.1 If the thermostat of the hotblock will not maintain temperature or cannot be calibrated against the NIST traceable thermometer, discontinue using it. Tag the hotblock as “out of service” and notify the Quality Control Department and the Department Manager/Supervisor.

11.2 Air displacement pipettes and bottle top dispensers must be verified on a quarterly basis.

11.3 Whenever a box of PDVs with a new lot number is opened, the PDVs must be checked for precision.

11.3.1 The PDVs must be checked at 10.0, 25.0, and 50.0mL.

11.3.2 The calibration verification sheet will be kept with the volume certification sheet sent by Environmental Express® in a binder in the Metals Department.

12. Procedure

12.1 Identify the aqueous samples to be prepared for ICP analysis.

12.1.1 If the sample is from a client who requires an internal chain of custody, fill out the internal chain of custody logbook for the Metals Department.

12.2 Turn on the hotblock and let it warm up to pre-determined temperature with will bring the samples to a temperature of 95±2°C.

12.2.1 The actual temperature of the hotblock is measured with a NIST traceable thermometer that is suspended in a PDV filled with water.

12.2.2 The temperature of the hotblock is to be adjusted so that the temperature of the water in the PDV which contains the NIST thermometer measures 95±2°C. Record that the temperature is within the appropriate temperature range on the ICP metals digestion bench sheet.

12.3 Separate the samples into batches according to Epic Pro Acodes.

12.3.1 Determine whether the dissolved samples have been field filtered (marked Dissolved Metals and already acidified) or if they need to be lab filtered (not acidified).

12.3.1.1 For samples that require lab filtration, fill a 100mL PDV with the sample, attach the 100mL PDV to a flipmate filter and filter the sample by vacuum filtration.

12.3.1.2 When the sample filtration is completed, pour the filtrate into a bottle containing 1mL of concentrated trace grade nitric acid.

12.3.1.2.1 If the original sample bottle is not visibly stained, rinse it out with reagent water and acidify it with 1mL of concentrated trace metal grade nitric acid.

12.3.1.2.2 If the original sample bottle is visibly stained, keep the sample in the 100mL PDV and acidify it with 1mL of concentrated trace metal grade nitric acid.

12.4 Record the sample identifications in the appropriate aqueous ICP logbook (liquid or liquid-recoverable). Complete all requested information.

12.4.1 In the open space where the initial volume is recorded, in parenthesis, write down the number corresponding to the sample bottle that was used.

12.5 For each sample, write the sample identification number and preparation date on a PDV and place them in a hotblock rack.

12.5.1 A “R” after the identification number designates the sample as a recoverable metals sample.

12.5.2 A “D” after the identification number designates the sample as a dissolved metals sample.

12.5.3 A “P” after the identification number designates the sample as a TCLP sample.

12.5.4 A “S” after the identification number designates the sample as a SPLP sample.

12.6 The following QC samples must be analyzed with each batch of 20 samples:

12.6.1 One method blank per 20 samples (DI Water).

12.6.2 One LCS per 20 samples.

12.6.3 One MS per 10 samples.

12.6.4 One Duplicate per 10 samples.

12.6.5 One MSD per 20 samples.

12.7 Shake each sample well and immediately pour a 50mL aliquot of the sample into the corresponding PDV.

12.7.1 If a sample contains a slight oil layer that would cause it to boil over or a lot of sediment, a reduced volume may be used.

12.7.1.1 If a reduced volume is used (i.e., 1mL or 10mL of sample), bring the sample up to 50mL in the PDV with DI water before adding the acid.

12.7.2 Water sample preservation must be verified to be at a pH of <2 prior to taking an aliquot for digestion or analysis.

12.7.3 For each DUP sample, write the same sample identification number and prep date on two PDVs.

12.7.3.1 On one of the PDVs, add the letters DUP after the sample identification.

12.7.4 For each MS and MSD sample, write the same sample identification number and prep date on three PDVs.

12.7.4.1 On one of the PDVs, add the letters MS after the sample identification.

12.7.4.2 On another PDV add the letters MSD after the sample identification.

12.7.4.3 Pipette 0.125mL of each of the Inorganic Ventures PA Standard solutions into each sample labeled as an MS or MSD.

12.7.5 For each LCS sample prepared with every batch of samples, label a PDV as LCS

12.7.5.1 Add 50mL of reagent water to a PDV labeled as LCS.

12.7.5.2 Pipette 0.125mL of each of the Inorganic Ventures PA Standard solutions and the sulfur standard into each sample labeled as LCS.

12.7.5.3 If the sample is for dissolved metals, a filtered LCS must be digested.

12.7.5.3.1 Fill a clean 250mL bottle with 200mL of DI water, pipette 0.5mL of each of the Inorganic Ventures PA Standard solutions and the sulfur standard into the DI, add 10mL of HCl and 4mL of HNO_3 to the solution and filter.

12.7.5.3.2 Label the clean 250mL bottle with the lot number of the flipmate filter, the reagent numbers of the acids, the standards identification numbers, and the date.

12.7.5.3.3 Pour 50mL of the solution into a PDV labeled as the LCS for any dissolved samples being digested, place it in the hotblock and digest according to the method.

12.7.6 For each method blank sample prepared with every batch of samples, label a PDV as MB (or PB for preparation blank)

12.7.6.1 Add 50mL reagent water to each PDV labeled as MB/PB.

12.7.6.2 If the sample is for dissolved metals, a filtered MB/PB must be digested.

12.7.6.2.1 Fill a clean 500mL bottle with DI water and filter the water.

12.7.6.2.2 Add 2mL of concentrated HNO_3 to the DI water.

12.7.6.2.3 Label the clean 500mL bottle with the lot number of the flipmate filter, the reagent number of the HNO_3, and the date.

12.7.6.2.4 Add 50mL of the filtered DI to the PDV labeled as the MB/PB for any dissolved samples being digested.

12.8 In a hood add the following to each sample;

12.8.1 The samples that will be analyzed for total, dissolved, TCLP, SPLP, and ASTM metals are recorded in the liquid ICP logbook. To each sample add:

12.8.1.1 2.5mL concentrated HCl.

12.8.1.2 1.0mL concentrated HNO_3.

12.8.1.2.1 Record the volumes of HNO_3 and HCl added to each sample in the preparation logbook.

12.8.1.2.2 Attachments 1 and 2 provide examples of the logbooks that are used for this preparation method.

12.8.2 The samples that will be analyzed for recoverable metals are recorded in the liquid-recoverable ICP logbook. To each sample add:

12.8.2.1 1.0mL concentrated HNO_3

12.8.2.1.1 Record the total volume of HNO_3 added to the sample in the preparation logbook.

12.8.2.2 This digestion procedure is specific to West Virginia clients.

12.9 Place the rack containing the PDVs into the hotblock.

12.10 Heat the samples at 95±2°C, until the volume is reduced to under 20mL (about 4-5 hours).

12.10.1 Any batch that contains samples for analysis by EPA Method 200.7 must be capped (PDV with the hole) and refluxed for 30 minutes after the volume has been reduced.

12.11 Remove the racks from the hotblock and allow the samples to cool to room temperature.

12.12 Dilute the samples to a final volume 50mL with reagent water.

12.12.1 Allow any undissolved material to either settle overnight, or centrifuge a portion of the sample.

12.13 Tightly cap the PDVs and invert each two or three times to mix the digested sample and the reagent water.

12.14 Submit the samples and a copy of the ICP preparation logbook(s) page(s) to the instrument lab for analysis.

13. Calculations

13.1 See the Pace Analytical Services, Inc. Quality Assurance Manual for commonly used calculations.

14. Quality Control

14.1 Each batch of samples shall have at a minimum the following QC samples:

14.1.1 One Method Blank (MB).

14.1.2 One Laboratory Control Sample (LCS).

14.1.3 Two Matrix Spikes (MS).

14.1.3.1 Prepared using two different samples. The first MS is to be prepared from one of the first 10 samples in the batch and the second MS is to be prepared from one of the 2nd 10 samples in the batch.

14.1.4 Two Duplicate Samples (DUP)

14.1.4.1 Prepared using two different samples. Prepared from the same samples as those used for the MS.

14.1.5 One Matrix Spike Duplicate (MSD)

14.1.5.1 Prepared using the same sample as the first MS sample of the batch.

14.2 Corrective Actions for Out-Of-Control Data

14.2.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.2.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.2.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results noted in the final report.

14.2.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.2.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.2.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.2.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.2.5.2 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their reporting limit, and duplicate precision meets the acceptance criteria.

14.2.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 An analyst shall not prepare samples by this method without supervision until they have completed training which requires that they:

15.1.1 Read and understand this SOP and referenced methods.

15.1.2 Complete an initial demonstration of capability (IDOC).

15.1.2.1 An IDOC consists of preparing four (4) LCS samples that when analyzed meet the required acceptance criteria.

15.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

16.2 All chemicals, reagents, and solutions should be used in a hood.

16.3 Keep the volume of the solutions to the smallest amount needed to accomplish the task at hand. This will minimize the amount of solution spilled if the flask or PDV is accidentally broken or knocked over.

16.4 Use funnels when pouring solutions to avoid splashing or spills.

16.5 Where possible, dispense acids and solutions in bottles with a bottle top dispenser to avoid splashing or spills.

16.6 All solutions, chemicals, and reagents used or generated during this procedure must be disposed of in compliance with all regulations and requirements and the laboratory's waste handling and disposal policy.

17. References

17.1 USEPA, An Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy. Method 3005A Revision 1, July 1992.

17.2 T. D. Martin, C. A Brockhoff, J. T. Creed, and EMMC Methods Work Group – Method 200.7, Revision 4.4 (1994).

17.3 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.4 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.5 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.6 SOP PGH-C-032, Support Equipment, current version.

17.7 SOP PGH-C-035, MDL-LOD, current version.

17.8 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.9 SOP PGH-Q-038, Laboratory Equipment, current version.

17.10 SOP S-ALL-Q-011, Audits, current version.

17.11 SOP S-ALL-Q-012, Corrective Action, current version.

17.12 SOP S-ALL-Q-020, Training, current version.

17.13 SOP S-ALL-Q-028, Lab Track, current version.

17.14 SOP PGH-C-027, DI Water, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Figure #1: Flowchart for the preparation of ICP samples in an aqueous matrix.

18.2 Table #1: Potential problems that may occur with the process of this SOP and corrective actions.

18.3 Attachment No. 1: ICP Digestion Logbook (Example).

19. Revisions

Document Number	Reason for Change	Date
PGH-M-015-6	1. Added to Section 8.3.3.1: After the sample is verified to be pH <2, make a note in the comment section of the prep logbook that the pH <2. 2. Added to Section 12.7.1 added about use of reduced volume. 3. Section 12.8.2.2: This digestion procedure is specific to West Virginia clients. 4. Added to Section 21.6: For site specific West Virginia clients, only 1mL of HNO_3 is added to the sample instead of 2.5mL of HCl and 1mL of HNO_3. 5. Added updated digestion form.	06Mar2014
PGH-M-015-7	1. Removed Section 12.8.1.3 regarding drinking water. 2. Removed references to drinking water.	13Mar2014
PGH-M-015-8	1. Edited for grammar and spelling. 2. Added Section 12.8.1.2.1: 'Record the volumes of HNO_3 and HCl added to each sample in the preparation logbook. 3. Updated Attachments 1 and 2. 4. Document Reformatted. 5. Added SOP references. 6. Updated digestion sheets added.	15Jul2014

20. Maintenance

20.1 Replace fuse in the hotblock when necessary.

20.2 Replace battery in the thermometer when necessary.

20.3 Clean the bottle top dispenser when necessary.

20.4 See Table #1.

21. Method Modifications

21.1 The Environmental Express® hotblock and polyethylene digestion vessels (PDV) are used to digest the samples in place of the hotplate and glass beakers listed in the method.

21.2 Instead of using an aliquot of 100mL of sample in the glass beakers, an aliquot of 50mL of sample is used in the PDVs.

21.3 19.2.1 An aliquot of less than 50mL may be used for samples with problematic matrices if it is noted in the comment section on the prep page.

21.4 Differences in acid volumes: (adjusted for use in the PDVs)

21.4.1 1.0mL of HNO_3 is used instead of 2.0mL.

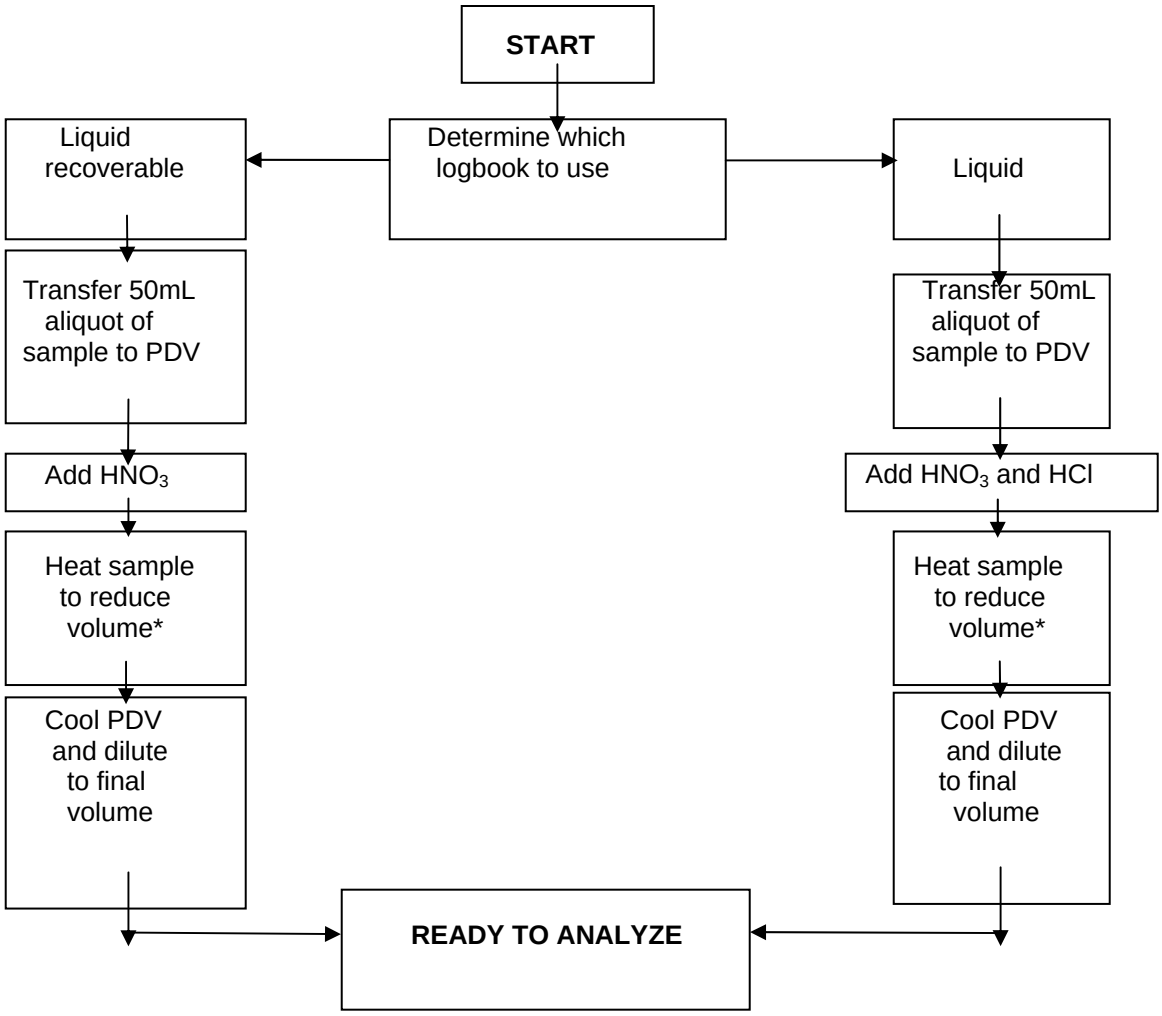
21.4.2 2.5mL of HCl is used instead of 5.0mL.

21.5 After the sample has been reduced to a volume of 20mL, it is diluted back up to a volume of 50mL in the PDV instead of 100mL in a glass flask.

21.6 For site specific West Virginia clients, only 1mL of HNO_3 is added to the sample instead of 2.5mL of HCl and 1mL of HNO_3.

21.7 The list of metals (analytes) in section 2.3 includes boron and silicon (as silica). These are not included in the analyte list for Method 3005A, but they are included in the analyte for EPA 200.7.

Figure #1



* Samples by 200.7 require 30 minute reflux after volume reduction.

Table #1

	Potential Problems	Corrective Actions
Using hotblock and PDVs	Hotblock needs to be repaired or low Supply of PDVs	Use hotplate and Beakers
Adding to liquid: 2.5mL HCl 1.0mL HNO_3 -per 50mL aliquot	Hotblock needs repaired or low Supply of PDVs	Add to liquid: 5.0mL HCl 2.0mL HNO3 - per 100mL aliquot
Adding to liquid-recoverable: 1.0mL HNO_3 -per 50mL aliquot	Hotblock needs repaired or low Supply of PDVs	Add to liquid-recoverable 2.0mL HNO_3 -per 100mL aliquot

Attachment No. 1

Example ICP Metals Aqueous Digestion Sheet

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Pace Analytical Services, Inc.- Pittsburgh

ICP Aqueous Metals Digestion Sheet/ Method EPA 3005A

Logbook ID: 1-M005-7 **SOP ID: PGH-M-015**

Batch#:_____ HCl IDI#:_____

Analyst:_____ HNO3 ID#:_____

Prep Date:_____ LCS/SPIKE ID#:_____

Digestion Vessel Lot#:_____

Thermometer ID & Digestion Block ID: _____ Position: _____

Temp Limits 93-97° C Observed Temp._____°C Correction Factor_____°C Final Temp._____°C

Temperature Adjusted: Yes____ No:_____ Start Time: _____ End Time: _____

Dissolved Metals:

Filter Lot ID#: _____ Filter Vessel Lot ID#: _____ HNO_3 Lot #: _____

Project	Sample ID	Initial Volume (mL)	Final Volume (mL)	Acid Used (mL) HNO3	Acid Used (mL) HCl	Comments
	PB ( )					
	LCS ( )					
	DUP					
	MS					
	MSD					
	DUP					
	MS					

Peer Review_____

Attachment 2

Example ICP Metals Digestion Sheet

Recoverable-Aqueous Samples

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Pace Analytical Services, Inc.-PGH

ICP Metals Digestion Sheet (Recoverable-Aqueous)/Method EPA 3005A

Logbook ID: 1-M006-7

SOP ID: PGH-M-015

Prep Date : _____ Batch#:_____ HNO3 ID#:_____

Analyst:_____ LCS/SPIKE ID#:_____

Digestion Vessel Lot #_____

Thermometer ID & Digestion Block ID # : _____ Position ID: _____

Temp Limits: 93-97 °C Observed Temp._____°C Correction Factor_____°C Final Temp._____°C

Temperature Adjusted: Yes____ No:___ Start Time: _____ End Time: _____

Project	Sample ID	Initial Volume (mL)	Final Volume (mL)	Acid Used (mL) HNO3	Comments
	PB ( )				
	LCS ( )				
	DUP				
	MS				
	DUP				
	MS				

Peer Review: _____

STANDARD OPERATING PROCEDURE

Preparation Solid/ Semi Solid Samples for ICP Analysis
Method: 3050B

SOP NUMBER:	PGH-M-013-7
REVIEW:	M. Kruth and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-M-013-6
REVIEW DATE:	Upon Procedural Change

APPROVALS

Marla L. Kruth

Assistant General Manager — 06/27/14 Date

Maureen K. DeRubeis

Senior Quality Manager — 07/15/14 Date

Department Manager/Supervisor — 07/15/14 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

1. Purpose

   1.1 This SOP documents the procedure to be followed for the sample digestion of sediment, sludge, soils, and wipes for metals analysis by ICP-AES using EPA Method 3050B.

2. Scope and Application

   2.1 This procedure applies to samples that are sediments, sludge, soils, and wipes.

3. Summary of Method

   3.1 A weighed portion of sample or one wipe is refluxed in a 1:1 HNO_3 solution for 10 minutes at 95±5°C in a hotblock.

   3.2 The sample is removed from the hotblock, cooled, and concentrated HNO_3 is added to it. The sample is placed back in the hotblock and refluxed for an additional 30 minutes.

   3.3 The sample is then removed from the hotblock, cooled, and reagent (DI) water and hydrogen peroxide are added. The sample is placed back in the hotblock and heated.

   3.4 Additional volumes of hydrogen peroxide are added to the sample while heating, until all bubbling subsides.

   3.5 Reduce the volume of the sample to about 5mL.

   3.6 Cool the sample and add concentrated HCl. The sample is placed back in the hotblock and refluxed for 15 minutes.

   3.7 The sample is diluted to 50mL with DI water and submitted for analysis.

4. Interferences

   4.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge.

   4.2 Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Section 8.0 of Method 3050B to aid in determining whether Method 3050B is applicable to a given waste.

5. Safety

   5.1 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be performed in a fume hood.

   5.2 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

   5.3 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a

potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.4 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 Batch: A set of no more than 20 samples, each of which is a well mixed, homogeneous representative portion of a sample.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

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7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine for Method 3050B.

8.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable.

8.3 Non-aqueous samples should be refrigerated at ≤6°C upon receipt and analyzed as soon as possible. Hold time is 180 days for all samples except where Hg must be analyzed. If Hg analysis is required, the sample must be analyzed within 28 days.

8.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce sample variability as long as drying does not affect the extraction of the analytes of interest.

9. Equipment and Supplies

9.1 Environmental Express™ Hotblock, or a temperature adjustable hotplate, or equivalent.

9.2 Disposable Polypropylene Digestion Vessels (PDV) with caps, or 250mL glass beakers with ribbed watch glasses.

9.3 Environmental Express™ Hotblock Rack, or equivalent.

9.4 Thermometers: Traceable to NIST Calibration and capable of measuring 95±5ºC.

9.5 Class A and Air Displacement Calibrated Pipettes, assorted volumes, Class A, glass.

9.6 Volumetric Flasks and Graduated Cylinders, Class A, glass.

9.7 Fisherbrand® Wooden Tongue Depressors, or equivalent.

9.8 Analytical Balance, Mettler with accuracy of ± 0.01g, or equivalent.

9.9 Nalgene® wash bottle.

9.10 Polypropylene beads, or equivalent.

10. Reagents and Standards

10.1 To prepare 1:1 HNO_3: Fill an empty, clean HNO_3 acid bottle with 1000mL DI water and slowly add 1000mL concentrated HNO_3 to it.

10.2 Record all the identifications information for all standards and solutions in the metals standard logbook and on the container used to store the solution. (See Attachment No.1).

10.3 Reagent (Millipore Type II) Water (DI water), refer to PGH-C-027, DI Water for water quality requirements.

10.4 Nitric Acid (HNO_3)- Fisher Scientific, or equivalent..

10.5 Hydrochloric Acid (HCl): Fisher Scientific, or equivalent.

10.6 Hydrogen Peroxide, 30% (H_2O_2)- Fisher Scientific Certified A.C.S., or equivalent.

10.7 Inorganic Ventures PA-Standard 1B (or equivalent). See the Certificate of Analysis and/or the Standard Preparation logbook for the solution contents and concentrations.

10.8 Inorganic Ventures PA - Standard 2B (or equivalent). See the Certificate of Analysis and/or the Standard Preparation logbook for the solution contents and concentrations.

10.9 Inorganic Ventures PA - Standard 3B (or equivalent). See the Certificate of Analysis and/or the Standard Preparation logbook for the solution contents and concentrations.

10.10 Solid beads: Environmental Express™, or equivalent.

10.11 For relevant information, such as purity, storage conditions, and expiration dates for standards, chemicals, and reagents refer to the Certificate of Analysis located in the laboratory.

11. Calibration

11.1 The temperature of the hotblock will be calibrated against a thermometer that is NIST traceable to verify the temperature of the solution in the PDV.

11.1.1 If the thermostat of the hotblock will not maintain temperature or cannot be calibrated against the NIST traceable thermometer, discontinue using it. Tag the hotblock as “Out of Service” and notify the Quality Department and the Department Manager/Supervisor.

11.2 The air displacement pipettes and bottle top dispensers must be verified on a quarterly basis.

11.3 Whenever a box of PDVs with a new lot number is opened, the PDVs must be checked for precision.

11.3.1 The PDVs must be checked at 10.0, 25.0, and 50.0mL.

11.3.2 The calibration verification sheet will be kept with the volume certification sheet sent by Environmental Express in a binder in the Metals Department.

12. Procedure

12.1 Identify the solid samples to be prepared for ICP analysis and retrieve them from sample storage.

12.1.1 If the sample is from a client that requires an internal chain of custody, fill out the internal chain of custody logbook for the Metals Department.

12.2 Turn on the hotblock and let it warm up.

12.2.1 The actual temperature of the hotblock is measured with an NIST thermometer that is suspended in a PDV filled with water.

12.2.2 The temperature of the hotblock is adjusted so that the temperature of the water in the PDV which contains the NIST thermometer measures 95±5°C.

12.3 Record the sample identifications in the solid ICP digestion logbook. Complete all requested information. (See Attachment No.2).

12.3.1 In the open space where the initial mass is recorded, in parenthesis, write down the number corresponding to the sample bottle that was used.

12.4 For each sample, write the sample identification number and preparation date on a PDV and place them in a hotblock rack.

12.5 Weigh a 0.5-1.0 ±0.01g portion of each sample into the corresponding PDV.

12.5.1 For a wipe sample, place the entire wipe into the corresponding PDV.

12.5.2 For the duplicate (DUP) sample, write the same sample identification number and prep date on two PDVs.

12.5.2.1 On one of the PDVs, add the letters DUP after the sample identification.

12.5.2.2 Weigh 0.5 to 1.0.g of sample into each PDV. Record the mass to the nearest hundredth (0.01g).

12.5.3 For the matrix spike (MS) sample, write the same sample identification number and prep date on two PDVs.

12.5.3.1 On one of the PDVs, add the letters MS after the sample identification.

12.5.3.2 Weigh 0.5 to 1.0g of sample into each PDV. Record the mass to the nearest .01g.

12.5.3.3 Using an air displacement pipette: Pipette 0.125mL of each of the three Inorganic Ventures™ standard solutions into the sample labeled as the MS.

12.5.4 Prepare a Laboratory Control Sample (LCS) sample with every batch of samples.

12.5.4.1 Label a PDV as LCS.

12.5.4.2 Add 0.5-1.0g of the polypropylene beads to the PDV labeled as LCS and pipette 0.125mL of each of the three Inorganic Ventures™ standard solutions into the PDV.

12.5.5 Prepare a Preparation Blank (PB) sample with every batch

12.5.5.1 Add 0.5-1.0g of the polypropylene beads and 5mL 1:1 HNO_3 to a PDV labeled as PB.

12.6 In a hood add 5mL 1:1 HNO_3 to each PDV and mix the slurry by gently swirling.

12.6.1 For a wipe sample, additional 1:1 HNO_3 will need to be added to each PDV because the wipe absorbs the initial 5mL of 1:1 HNO_3.

12.6.1.1 Any additional 1:1 HNO_3 that is added to a wipe sample will be noted in the comment section of the prep page.

12.7 Place a reflux cap on the PDV and reflux the samples at 95±5°C for 10 minutes in the hotblock.

12.8 After 10 minutes, remove the rack containing the samples from the hotblock, place them in the hood and let them cool for approximately 10-15 minutes.

12.9 Add 2.5mL concentrated HNO_3 to each PDV and return them to the hotblock to reflux for another 30 minutes.

12.9.1 If brown fumes are generated (indicating oxidation of the sample by the HNO_3), repeat this step with the addition of 5mL of concentrated HNO_3 repeating until brown fumes are no longer given off by the sample. This indicates that the reaction with the HNO_3 is complete.

12.10 Remove the rack containing the samples from the hotblock and place them in the hood to cool.

12.11 When the samples are cool, add 1mL DI water and 1.5mL 30% H_2O_2 to each PDV and return them to the hotblock.

12.12 Heat the samples until all effervescence subsides, then remove the samples from the hotblock and allow them to cool.

12.12.1 Continue to add 1mL aliquots of 30% H_2O_2 to the sample(s) while warming them until the effervescence is minimal or until the general sample appearance is unchanged.

12.12.2 Do NOT add more than a total of 5mL 30% H_2O_2 to any one sample.

12.13 Heat the acid-peroxide digestate in the hotblock for 40 minutes, or until the volume is less than 5mL. Remove the rack containing the samples from the hotblock and allow them to cool in the hood.

12.14 Add 5mL concentrated HCl to all of the PDVs and return them to the hotblock. Allow them to reflux for 15 minutes at 95±5°C.

12.14.1 Record the volumes of HNO_3 and HCl added to each sample in the preparation logbook.

12.15 Remove the rack with the samples from the hotblock and place them in the hood to cool.

12.16 Dilute the samples back up to a final volume of 50mL with DI water.

12.17 Cap the PDVs tightly and invert two or three times to mix the digested sample and the DI water.

12.18 Submit the samples and a copy of the ICP preparation logbook page(s) to the instrument lab for analysis.

12.18.1 Any solids present in the sample after the digestion process should be allowed to settle prior to the removal of an aliquot of the digestate for analysis.

13. Calculations

13.1 Results are reported on an “as received” basis. A percent solids determination must be performed if results based on dry weight are required.

13.1.1 The percent solids determination must be performed on a homogeneous aliquot of the sample.

14. Quality Control

14.1 Each batch of 20 or fewer samples shall have at a minimum the following QC samples;

14.1.1 One Prep Blank (PB).

14.1.2 One LCS.

14.1.3 One Matrix Spike (MS).

14.1.4 One Duplicate Sample (DUP).

14.2 The analytical balance must be checked for accuracy.

14.3 The air displacement pipettes must be checked for accuracy.

14.4 Corrective Actions for Out-Of-Control Data

14.4.1 Method Blank (Reagent Blank) (MB/RB): Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.4.2 Duplicate (DUP): DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.4.3 Matrix Spike Recovery (MS): MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported, the results noted in the final report.

14.4.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.4.4 Matrix Spike Duplicate (MSD): If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.4.5 Laboratory Control Sample (LCS): If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.4.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.4.6 Laboratory Control Sample Duplicate (LCSD): If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.4.6.1 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit, and duplicate precision meets the acceptance criteria.

14.4.7 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 An analysts shall not prepare samples by this method without supervision until they have completed training which requires that they;

15.1.1 Read and understand this SOP and referenced methods.

15.1.2 Complete an initial demonstration of capability (IDOC).

15.1.2.1 An IDOC consists of preparing four (4) LCS samples that when analyzed meet the required acceptance criteria.

15.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

16.2 All chemicals, reagents, and solutions are to be used in a hood.

16.3 Keep the volume of the solutions to the smallest amount needed to accomplish the task at hand. This will minimize the amount of solution spilled if the PDV or flask is accidentally knocked over or broken.

16.4 Use funnels when pouring solutions to avoid splashing or spills.

16.5 Where possible, dispense acids and solutions in bottles with a bottle top dispenser to avoid splashes or spills.

16.6 All solutions, chemicals, and reagents used or generated during this procedure must be disposed of in compliance with all applicable regulations and requirements and the laboratory's waste handling and disposal policy.

17. References

17.1 USEPA, An Acid Digestion of Sediments, Sludges, and Soils for Analysis by FLAA or ICP Spectroscopy. Method 3050B Revision 2, December 1996.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.3 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.4 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.5 Pace Analytical Services, Inc. SOP PGH-M-008, current version.

17.6 SOP PGH-C-032, Support Equipment, current version.

17.7 SOP PGH-C-035, MDL-LOD, current version.

17.8 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.9 SOP PGH-Q-038, Laboratory Equipment, current version.

17.10 SOP S-ALL-Q-011, Audits, current version.

17.11 SOP S-ALL-Q-012, Corrective Action, current version.

17.12 SOP S-ALL-Q-020, Training, current version.

17.13 SOP S-ALL-Q-028, Lab Track, current version.

17.14 SOP PGH-C-027, DI Water, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Figure #1: Flowchart for the preparation of ICP samples in a solid or semi-solid matrix.

18.2 Table #1: Potential problems that may occur with the process of this SOP and corrective actions.

18.3 Attachment No.1: ICP Solid Digestion Logbook (Example)

19. Revisions

Document Number	Reason for Change	Date
PGH-M-013-3	1. Annual Review (2011): Updated Cover Sheet, Headers and Footers for this Revision, Added Signature line for Department Supervisor/Manager, Added Annual Review Signature lines (no changes). 2. Added wipe matrix to SOP (throughout document). 3. Section 10: Water Type and Vendor references changed. (10.2, 10.3, 10.4), Added solid matrix (10.10). 4. Section 11: Added verification of mechanical Pipettes (11.2), and PDVs (11.3). 5. Section 12: Added documentation of sample bottle ID (if more than one received) (12.4.1), Replaced all references to Teflon® chips with “solid beads”. 6. Added Revisions Section (Section 19). 7. Added Maintenance (Section 20). 8. Added Method Modifications (Section 21).	15Feb2011

Document Number	Reason for Change	Date
PGH-M-013-4	1. Added to Section 9.10: Polypropylene beads (or equivalent). 2. Added to Section 10.4 and 10.5: Fisher Scientific 3. Added Section 12.1.1: If the sample is from a client that requires an internal chain of custody, fill out the internal chain of custody logbook for the metals department. 4. Added to Sections 12.5.4.2& 12.5.5.1 the polypropylene.	26Mar2013
PGH-M-013-5	1. 12.5.4.2 Revised: …and pipette 0.125mL of each of the three Inorganic Ventures standard solutions into the PDV. 2. Updated references.	11Oct2014
PGH-M-013-6	1. Updated digestion form added to SOP.	06Mar2014
PGH-M-013-7	1. Added Table of Contents 2. General editing for grammar and spelling 3. Section 12.9.2: The following was added: Record the volumes of HNO_3 and HCl added to each sample in the preparation logbook. 4. Section 12.13: The digestion time was modified to be 40 minutes, or until the volume is less than 5 mL 5. Attachment 1 was updated to include acid volumes used. 6. Document Reformatted. 7. Added SOP references.	15Jul2014

20. Maintenance

20.1 Replace the fuse in the hotblock when necessary.

20.2 Replace the battery in the thermometer If/when necessary.

20.3 Clean the bottle top dispenser when necessary.

20.4 See Table #1.

21. Method Modifications

21.1 The Environmental Express hotblock and Polyethylene Digestion Vessels (PDV) are used to digest the samples in place of the hotplate and glass beakers listed in the method.

21.2 Instead of using a sample mass of 1-2 g in the glass beakers, a sample size of 0.5-1g is weighed out in a PDV.

21.3 Differences in acid and reagent volumes: (adjusted for use in the PDVs):

21.3.1 5.0mL 1:1 HNO_3 is used instead of 10mL.

21.3.2 2.5mL concentrated HNO_3 is used instead of 5mL.

21.3.2.1 If this step needs to be repeated because of brown fumes, 2.5mL concentrated HNO_3 is used instead of 5mL.

21.3.3 1.0mL DI and 1.5mL 30% H_2O_2 are used instead of 2mL DI and 3mL H_2O_2.

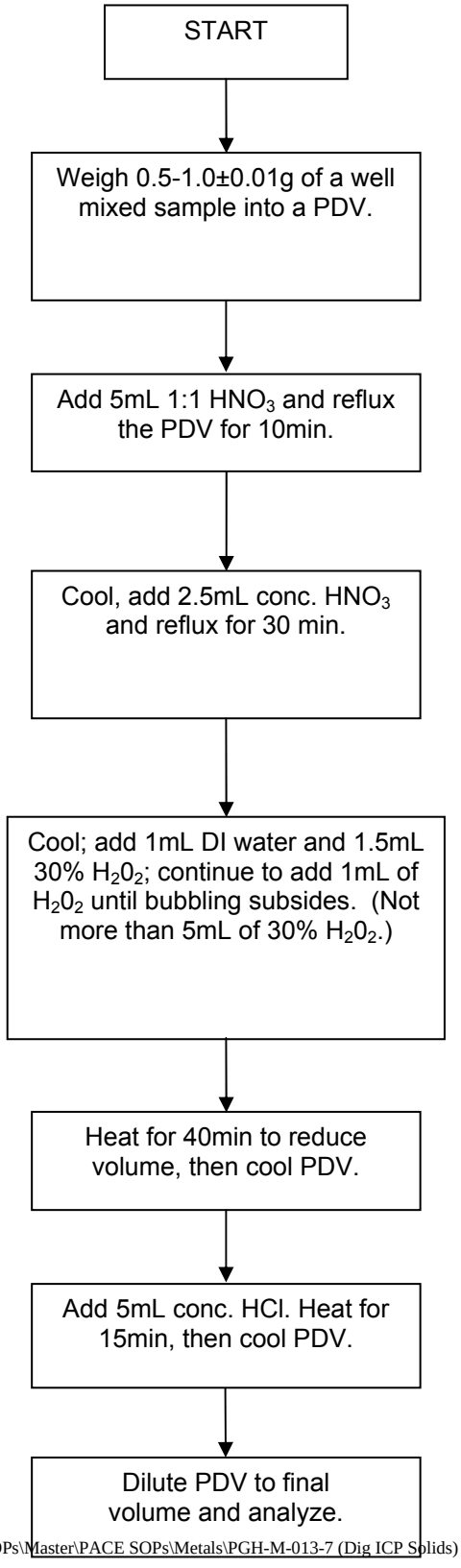
21.3.3.1 No more than a total of 5mL H_2O_2 will be added to any one PDV, instead of 10mL.

21.3.4 5.0mL concentrated HCl is used instead of 10mL.

21.3.5 After the sample has been reduced to a volume of less than 20mL, it is diluted back up to a volume of 50mL in the PDV instead of to 100mL in a glass flask.

21.4 Preparing wipes by this method constitutes a method modification as the matrix is not listed in EPA 3050B.

Figure #1


START
Weigh 0.5-1.0±0.01g of a well mixed sample into a PDV.
Add 5mL 1:1 HNO_3 and reflux the PDV for 10min.
Cool, add 2.5mL conc. HNO_3 and reflux for 30 min.
Cool; add 1mL DI water and 1.5mL 30% H_20_2; continue to add 1mL of H_20_2 until bubbling subsides. (Not more than 5mL of 30% H_20_2.)
Heat for 40min to reduce volume, then cool PDV.
Add 5mL conc. HCl. Heat for 15min, then cool PDV.
Dilute PDV to final volume and analyze.

Attachment 1

Example ICP Metals Solid Digestion Logbook

Method 3050B

Pace Analytical Services, Inc.-PGH 1 of 50

ICP Solid Metals Digestion Sheet/Method EPA 3050B

Logbook ID: 1-M004-9

SOP ID: PGH-M-013

LCS/SPIKE ID#:_____

Batch #: _____ HCl IDI#:_____ Solid QC (LCS) ID#:_____

Analyst:_____ HNO3 ID#:_____ Hydrogen Peroxide ID#:_____

Prep Date:_____ 1:1 HNO3 ID#:_____ Digestion Vessel Lot#_____

Temp Limits 90-100^0 C Observed Temp._____^{0}C Correction Factor_____^{0}C Final Temp._____^{0}C

Temperture Adjusted: Yes____ No_____ Start Time: _____ End Time: _____

Balance ID: XS203S ____ PG503S ____ ML802E ____

Thermometer ID & Digestion Block ID: _____ Position: _____

Project	Sample ID	Initial Weight (g)	Final Volume (mL)	Acid Used (mL) 1:1 HNO3	Acid Used (mL) Conc.: HNO3	Acid Used (mL) Conc.:HCl	Comments
	PB ( )						
	LCS ( )						
	DUP						
	MS						

Peer Review: _____

STANDARD OPERATING PROCEDURE

Metals and Trace Elements in Waters, Wastes and Solids by ICP-AES
by EPA Methods 200.7, 6010B and 6010C

SOP NUMBER:	PGH-M-008-16
REVIEW:	N. DeRubeis & Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-M-008-15
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	7/7/15 Date
Senior Quality Manager	7/7/15 Date
Department Manager/Supervisor	7/7/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This SOP documents the procedure to be used for the Determination of Metals and Trace Elements in Waters, Wastes and Solids Matrices using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) by EPA Methods 200.7, 6010B, and 6010C.

2. Scope and Application

2.1 This procedure is used to determine the concentration of metals and some non-metals in surface, saline waters, domestic, industrial waste waters and solid samples.

2.2 This procedure is also used to determine the concentration of metals in mobility procedure extracts (TCLP, ASTM, SPLP).

2.3 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used to determine metals and some nonmetals in solution. This procedure is a consolidation of existing methods for water, wastewater, and solid wastes. This procedure is applicable to the following analytes:

Aluminum	Copper	Selenium
Antimony	Iron	S_1O_2
Arsenic	Lead	Silver
Barium	Lithium	Strontium
Beryllium	Magnesium	Thallium
Boron	Manganese	Tin
Cadmium	Molybdenum	Titanium
Calcium	Nickel	Vanadium
Chromium	Phosphorus	Zinc
Cobalt	Potassium	Zirconium[(b)]
Silicon[(b)]	Sodium	Sulfur[(b)]

(a) This procedure is not suitable for the determination of silica in solids.
(b) Zirconium, silicon, and sulfur are analytes that are not included in EPA 6010C or EPA 200.7.

2.3.1 Additional elements may be analyzed by this procedure provided they are developed (i.e., Linear Ranges, LOD, DOCs, IEC's, etc.) and the documentation is on file.

2.4 ICP-AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v).

2.5 With the exception of silver, where this procedure is approved for the determination of certain metal and metalloid contaminants in waste water, aqueous samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has a turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis."

2.6 For the determination of total recoverable analytes in aqueous, biosolids, and solid samples, a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soil, biosolids, sediment, and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing total suspended solids >1% (w/v) should be extracted as a solid sample.

2.7 The reporting limits for water and soil are listed in Table 1.

3. Summary of Method

3.1 An aliquot of a well-mixed, homogeneous sample is accurately weighed or measured for sample processing.

3.1.1 For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are solubilized by gentle refluxing with HNO_3 and HCl.

3.1.2 For the total recoverable analysis of a biosolids sample containing <1% total suspended solids, analytes are solubilized by successive refluxing with HNO_3 and HCl.

3.1.3 For total recoverable analysis of a biosolids sample containing total suspended solids >1% (w/v), analytes are solubilized by refluxing with HNO_3, background organic materials are oxidized with peroxide, and analytes are further solubilized by refluxing with HCl.

3.1.4 After cooling, the sample is brought to volume, mixed and then centrifuged or allowed to settle overnight prior to analysis.

3.2 The analysis described in this method involves multi elemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosols are transported to the plasma torch. Element specific emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. The background must be measured adjacent to an analyte wavelength during analysis. Interferences must be considered and addressed appropriately.

4. Interferences

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak.

4.1.2 Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other.

4.1.3 The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

4.2 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which

involves measuring the interfering elements. When operative and uncorrected, these interferences will produce false-positive determinations and will be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. More extensive information on interference effects at various wavelengths and resolutions is available in Boumans' Tables. Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

4.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

4.4 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from the known interferences, and to use a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must either be free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient.

4.5 All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrument change such as the type of torch, nebulizer, injector or plasma conditions occurs.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

5.3.1 Specifically, concentrated HNO_3 and HCl present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses with side shields for eye protection, and protective clothing. Observe proper mixing when working with these reagents.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification and digestion of samples must be performed in a fume hood.

5.5 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 Calibration blank: A volume of reagent water acidified with the same acid matrix as the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

6.3 Dissolved analyte: The concentration of an analyte in an aqueous sample that has been passed through a 0.45 μm membrane filter prior to sample acidification.

6.4 Inductively Coupled Plasma Spectrophotometer (ICP).

6.5 Instrument Detection Limit (IDL): The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicates of the calibration blank signal at the same wavelength.

6.6 Internal standard: Pure analyte(s) added to a sample, extract, or standard solution in a known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a target element.

6.7 Linear dynamic range (LDR): The concentration range over which the instrument response to an analyte is linear.

6.8 Initial Calibration Verification (ICV) solution: A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria. The ICV stock solution is obtained from a source external to the laboratory and different from the source of the calibration standards. This is also referred to as a Quality Control Sample (QCS).

6.9 Continuing Calibration Verification (CCV) solution: A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of criteria. This is prepared from the same source as the Calibration standards. The CCV is equivalent to Instrument Performance Check (IPC) solution.

6.10 Interference Check Samples (ICSA, ICSAB): A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences. This is equivalent to the Spectral interference check (SIC) solution.

6.11 Standard addition: The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the

sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

6.12 Interelement Correction Factor (IEC): Spectral interferences caused by background emission from continuous recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

6.13 Limit of Detection (LOD): An estimate of the minimum amount of an analyte in a matrix that the analytical process can reliably detect.

6.14 Demonstration of Capability (DOC): A procedure to demonstrate the ability of the analyst to generate analytical results of acceptable accuracy and precision.

6.15 Low level verification standard (CRDL /LLICV): A standard that is at the reporting limit and verifies the laboratories practical quantitation limit or reporting limit.

6.16 LLCCV: A standard that is at the reporting limit and verifies the laboratories practical quantitation limit or reporting limit. This is the same solution as the (CRDL /LLICV).

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to withdrawing an aliquot for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

8.1.1 NOTE: Do not dip pH paper or a pH meter directly into the sample; remove a small aliquot with a clean pipette and test the aliquot.

8.2 For the determination of the dissolved elements, a sample must be filtered through a 0.45μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus is recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical). Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to pH <2 immediately following filtration.

8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) HNO_3 to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient samples).

8.4 Any dissolved samples preserved in the laboratory must then be verified to be at pH <2 just prior to withdrawing an aliquot for processing or "direct analysis." Any 'Total Metals' sample preserved in the laboratory must be held for 24 hours, and then verified to a pH <2 prior to withdrawing an aliquot for processing or direct analysis. The Metals Prep department must verify the pH of the samples preserved in the laboratory at the time of sample preparation. The date and time (which is the same as the prep date and time) of the verification must be recorded on the prep bench sheet and verified to be at least 24 hours after the addition of the preservative which is done by Sample Receiving as documented on the SCUR (Sample Condition Upon Receipt) form.

8.4.1 If, for some reason such as high alkalinity, the 'Total Metals' sample pH is verified to be >2, more acid must be added and the sample is held for 24 hours until verified to be pH <2.

8.4.2 All additions of acid to samples by the laboratory to preserve samples are recorded in the sample preparation logbooks.

8.4.3 NOTE: When the nature of the sample is either unknown or is known to be hazardous, acidification should be performed in a fume hood.

8.4.4 A dissolved MB and LCS must be placed through the same process as the dissolved samples.

8.5 Solid samples require no preservation prior to analysis other than storage at 4°C if mercury analysis is also required. The recommended hold time for solids is 6 months from the date of collection.

9. Equipment and Supplies

9.1 Thermo Scientific 6500 Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES).

9.2 Computer loaded with appropriate software and attached printer.

9.3 Autosampler.

9.4 Assorted glass and air-displacement pipettes.

9.5 Assorted volumetric flasks, glass, Class A.

9.6 17 x 100 round bottom polystyrene culture tube or equivalent.

10. Reagents and Standards

10.1 See the Metals Department standard logbook for the specific procedures to be followed for the preparation of the standards listed below.

10.2 All standards are matrix matched with acid.

10.3 Fisher Trace metal grade concentrated HNO_3 or equivalent.

10.4 Fisher Trace metal grade concentrated HCl or equivalent.

10.5 Reagent DI water (ASTM Type II or equivalent).

10.6 Inorganic Ventures Custom Grade Multi-Element Standards. Currently for instrument calibration PA-STD 1B, PA STD 2B, PA STD 3B, or equivalent.

10.7 SPEX Custom Assurance Standards 1-3. or equivalent.

10.8 Various 1000 mg/L single element ICP grade standards, or equivalent.

10.9 Various 10,000 mg/L single element ICP grade standards, or equivalent.

10.10 10000 mg/L Yttrium for internal standard or equivalent.

10.11 10000 mg/L Indium for internal standard or equivalent.

11. Calibration

11.1 Single Point and Blank Calibration Procedure: The procedure for instrument calibration is typically a two point calibration performed with a blank and high calibration standard. This is then verified with an ICV, CCV and a CRDL. Any sample that is determined to be greater than the high calibration standard will be diluted and reanalyzed to be within the calibration range.

11.1.1 Other acceptable calibrations may be done at the request of a client or the analyst's discretion providing they meet acceptable verification criteria.

11.2 Multi-Point Calibration Procedure

11.2.1 The procedure for instrument calibration the analysis of three standards and a blank. The concentrations of the calibration standards are set to bracket the range of the expected sample concentrations with the third standard near the midpoint of the range.

11.2.2 The analytical sequence begins with the blank, then the three calibration standards in the order Low, Mid, High concentration.

11.2.3 A linear regression fit for the responses vs. the concentrations for the curve points is calculated.

11.2.3.1 A correlation coefficient ≥ 0.998 must be achieved for each element.

11.3 Table 3 lists calibration standards and concentrations.

11.3.1 See the Metals Department standard logbook for the specific instructions on how to prepare each standard used in this procedure.

12. Procedure

12.1 Inspect the instrument prior to igniting the plasma:

12.1.1 Inspect the sample introduction system. This will include:

12.1.1.1 Peristaltic pump tubing and all other tubing should be free of any visible debris. If there is any debris, change the tubing.

12.1.1.2 The nebulizer should be free of any visible debris. If there is any debris, remove the nebulizer and soak it in a 10 % HNO_3 solution. Remove it after 30 minutes and rinse it with de-ionized water. If the debris is still present, use compressed air or a thin wire in an attempt to dislodge the material. If this fails, install a new nebulizer.

12.1.1.3 The spray chamber should be clean. If not, remove the spray chamber and soak it in a 10 % HNO_3 solution. Use a test tube brush to remove any material that persists for more than 30 minutes.

12.1.2 Verify that the argon is on and that there is a sufficient quantity available for the projected analysis. A minimum pressure of 40 psi is required to ignite the plasma.

12.1.3 Verify that there is sufficient rinse solution (the rinse solution is approximately 2% HNO_3 and 5% HCl). The system will require approximately 1.5 L for each 8 hours of analysis time and is contained in a reservoir located under the autosampler.

12.1.4 Verify that there is sufficient capacity in the waste reservoir to prevent any overflow of acid waste from either the torch box or the autosampler's rinse station. If there appears to be insufficient capacity, use a siphon to remove excess acid waste. Dispose of the acid waste in the laboratory corrosives waste stream.

12.2 Igniting the plasma

12.2.1 Turn on the computer, monitor and printer. The computer will take approximately 30 seconds to boot up. When the login window appears, use the mouse to click on the CANCEL button. This will bring you into Windows®.

12.2.2 Double click on the iTEVA icon. The Thermo Scientific Page will appear.

12.2.3 On the bottom right of the page click on the PLASMA icon.

12.2.4 A panel will appear. Click on the PLASMA On button.

12.2.5 After the plasma lights click on the CLOSE button.

12.2.6 All gas flows and pump rates are automatically set.

12.3 Autosampler Setup:

12.3.1 Double click on the ANALYST icon

12.3.2 Select the current method.

12.3.3 Select the Sequence tab found in the lower left corner on the analyst window.

12.3.4 Click on AUTOSESSION located on the tool bar.

12.3.5 A window will appear. Select the NEW button.

12.3.6 Enter the number of samples to be analyzed and press the OK button.

12.3.7 On the tool bar select SEQUENCE.

12.3.7.1 Select LIST VIEW.

12.3.7.2 In the column labeled “Sample Name;” type the sample numbers in the order to be analyzed. No calibration or QC standards are required. These are designated by the method.

12.4 Instrument Calibration and Sample Analysis.

12.4.1 The calibration and sample analysis can be started by selecting the yellow triangle located on the tool bar.

12.4.2 To view the results:

12.4.2.1 Click on the Analyst tab located near the sequence tab.

12.4.2.2 Highlight NEW SAMPLES.

12.4.2.3 Analysis will continue until all samples are analyzed.

12.5 Instrument shutdown

12.5.1 When analysis is complete:

12.5.1.1 Close the Analyst window.

12.5.1.2 From the Thermo Scientific page Click on the PLASMA Icon.

12.5.1.3 A panel will appear, click on the PLASMA OFF button.

12.5.1.4 After approximately 1 minute, the instrument will complete the torch cool-down process.

12.5.1.5 Close all windows and turn off the computer.

13. Calculations

13.1 % Recovery

$$\%\,\mathrm{Recovery} = \frac{MeasuredValue}{TrueValue} \times 100$$

13.2 Hardness Calculation - Requires analytical results for the elements Calcium (Ca) and Magnesium (Mg).

Hardness, mg equivalent $CaCO_3$/L = (2.497 * [Ca, mg/L] + 4.118 * [Mg, mg/L])

13.3 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{SSR - SR}{SA} \right) \times 100$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

13.4 The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = \left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2} \right)} \right] \times 100$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

13.5 The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{CxV1xD}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

13.6 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg/Kg,dryweight = \frac{CxVxD}{WxS}$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight in Kg of wet sample digested

S = Percent solids/100

13.7 The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} x100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading $\times$ 5)

13.8 The final concentration determined in digested wipe samples is calculated as follows:

µg/wipe = (C x V x D x 1000)

Where:

C = Concentration (mg/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor

14. Quality Control

14.1 Corrective Actions for Out-Of-Control Data

14.1.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.1.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.1.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and the results noted in the final report.

14.1.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.1.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.1.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.1.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.1.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.2 Low Level Verification Standard (CRDL/LLICV): Standard prepared with the elements at the reporting limit. Analyzed after the ICSA/ICSAB during calibration. (See the concentrations of the Aqueous samples in Table #1).

14.3 Initial Calibration Verification (ICV): To be analyzed immediately following instrument calibration.

14.4 Initial Calibration Blank (ICB): To be analyzed immediately after the ICV.

14.5 Continuing Calibration Verification (CCV): To be analyzed after the CCB following the instrument calibration, and prior to any client samples.

14.6 Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB): to be analyzed at a frequency of one set for every 10 samples and at the end of the analytical sequence

14.7 Interference Check Samples (ICSA/ICSAB): Analyzed after the CCV during calibration. May be analyzed more often during the run after CCB's as needed.

14.8 Low Level Continuing Calibration Verification (LLCCV): Standard prepared with the elements at the reporting limit. Analyzed after the CCV at the end of the analytical sequence for Method 6010C. May be analyzed more often during the run after CCVs as needed.

14.9 Method Blanks (MB): One (1) per batch of 20 samples.

14.10 Laboratory Control Samples (LCS): One (1) per batch of 20 samples.

14.11 Duplicates (DUP): One DUP must be digested and analyzed with every 10 unknown samples. The MSD may be used as the duplicate if analyzed as part of the batch.

14.12 Matrix Spike (MS): One MS must be digested and analyzed with every 10 unknown samples.

14.13 Matrix Spike Duplicate (MSD): One MSD must be digested and analyzed with every batch of 20 samples analyzed for 6010B and 6010C.

14.14 Post Digestion Spike Test: As required by client specification, the PDST is to be analyzed upon the failure of MS/MSD. The same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same prep batch should be used as an alternative. Spike levels should produce expected recoveries within 10-100 times the RL for analytes of interest. Analyzed on a client specific basis.

14.15 Dilution Test: One per batch of 20 samples at a five-fold dilution as required by client specification. If the post digestion spike fails then a dilution tests should be run on the sample used for post digestion spike and MS/MSD. Multiple dilutions may be required by the client. Serial Dilution analyzed on a client specific basis. If both MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

14.16 Method of Standard Additions (MSA): Analyzed on a client specific basis. From USEPA Method 200.7, Rev 4.4, pages 34- 35:

"This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences such as contamination, inter element interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by the following:

$$\text{Sample Conc. (mg/L or mg/kg)} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

Where:

C = Concentration of the standard solution (mg/L)
S1 = Signal for fortified aliquot
S2 = Signal for unfortified aliquot
V1 = Volume of the standard addition (L)
V2 = Volume of the sample aliquot (L) used for MSA

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution."

15. Method Performance

15.1 In the event of a failure in any of the following Quality Control Sample requirements, corrective action should be taken in accordance with client specified requirements (or DQO). See the table in Section 15.16 for suggested corrective actions. In the event that a client has not provided/specified a DQO, corrective action shall be taken as outlined in Section 15.16.

15.2 ICV: Data for a specific element will not be accepted from an analytical run with an ICV that has a percent recovery that is greater than ±5% for samples analyzed according to USEPA Method 200.7 or ± 10% for samples analyzed using USEPA Method 6010B and 6010C. The %RSD of the replicate integrations must be < 5% for the elements of interest to be acceptable.

15.3 ICB: Data for a specific element will not be accepted from an analytical sequence which has a ICB which exceeds the reporting limit

15.4 CCV: Data for a specific element will not be accepted from an analytical batch were samples are not bracketed by CCV which have a percent recovery within ± 10% of the true value. The %RSD of the replicate integrations must be < 5% for the elements of interest to be acceptable.

15.5 CCB: Data for a specific element will not be accepted from an analytical batch were samples are not bracketed by CCBs which are less than the reporting limit or less than ½ the reporting limit for project that specify this in their quality plan.

15.6 MB: Method Blanks are acceptable when the result is less than the reporting limit or less than ½ the reporting limit for projects that specify this in their quality plan.

15.6.1 The concentrations of the elements in the client sample(s) are less than the reporting limit.

15.6.2 The concentrations in the client sample(s) are greater than ten (10) times the method blank contamination.

15.7 LCS: Must meet established control limits but cannot exceed ± 20 % of the true value.

15.7.1 Water samples are to be analyzed by EPA Method 200.7 criteria and must have a recovery within the range of ± 15 % of the true value for each element reported.

15.8 DUP: The %RPD between the sample and its duplicate must not exceed ± 20 % for elements of interest.

15.9 MS: The matrix spike recoveries must not exceed ± 25 % for elements of interest. If an (MS) and an (MSD) are analyzed the % RPD between the results must not exceed 20 %. If MS/MSD recoveries are unacceptable, the same sample used for MS/MSD should also be spiked with a post digestion spike as per client request. Recovery of post digestion spike must be within 80-120%.

15.10 ICSA/ICSAB: Elements present in either the ICSA or ICSAB must have a Percent Recovery of ± 10% of the established values for method 200.7 and ± 20% for methods 6010B and 6010C . Elements not present in either solution should not exceed ± 2 times the reporting limit, if an element of interest does exceed ± 2 times the reporting limit for 3 consecutive days the inter element correction factor should be evaluated.

15.11 CRDL/LLICV: Data for a specific element will not be accepted from an analytical batch with a CRDL/LLICV that has a percent recovery that is greater than ±50 % for samples analyzed according to methods 200.7 and 6010B and ±30 % for samples analyzed according to method 6010C.

15.12 LLCCV: Data for a specific element will not be accepted from an analytical sequence with a LLCCV that has a percent recovery that is greater than ±30 %.

15.13 Internal standards

15.13.1 If recovery of the internal standard is not within ± 50% for methods 200.7 and 6010B or ± 30% of the expected value for 6010C, the sample will be diluted and reanalyzed until the internal standard is within acceptable range.

15.13.2 Internal standard recovery limits must be met for project that specify the limits in their quality plan.

15.14 Linear Dynamic Ranges must be analyzed every six months or when major changes have been made to the analytical system.

15.14.1 The linear dynamic range is determined by analysis of standards at each wavelength used starting at the reporting limit and then standards at increasing concentrations, with a minimum of three standards being analyzed.

15.14.2 The procedure continues until the measured concentration of a standard differs from the actual concentration by more than 10%.

15.15 Dilution Test (Serial dilution): One per batch of 20 samples at a five-fold dilution as required by client specification. Multiple dilutions may be required by the client. Analyzed on a client specific basis. The 5X dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected

15.16 Corrective Actions

15.16.1 The following table shall be used as a guideline for evaluating samples/batches that have failed any QC requirements specified in Section 15. Client provided requirements should be consulted before determining a course of corrective action, as client specifications may deviate from the following guidelines.

QC Check	Frequency	Acceptance Criteria	Corrective Action
Two-point Initial Calibration [blank and 1pt] (ICAL)	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met.	RSD between duplicate exposures ≤ 5%.	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
Multi-point Initial Calibration [blank & 3pts] (ICAL)	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	Correlation Coefficient ≥ 0.998	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.

QC Check	Frequency	Acceptance Criteria	Corrective Action
MB	One per sample preparation batch of up to 20 samples.	< RL or if specified by project QAPP < ½ RL.	The method blank may be reanalyzed once in order to confirm potential contamination. The blank shall be considered contaminated upon failure of the acceptance criteria and the additional evaluation found in Section 15.6.1 – 15.6.2 , and all affected samples shall be re-digested. Samples failing the acceptance criteria but passing the additional evaluation found in section 15.6.1 – 15.6.2 may be reported if flagged appropriately.
ICV	Beginning of every analytical batch.	For 6010B and 6010C, ± 10% of true value. For 200.7, ± 5% of true value.	An ICV may be reanalyzed once. If the problem persists, correct the problem and recalibrate, then re-analyze all samples for any required analytes with unacceptable ICV recoveries.
CCV	Every 10 samples and at the end of the sequence.	Recoveries within ± 10% of expected value.	A CCV may be reanalyzed once. If the problem persists, correct the problem then re-analyze all samples for any analytes not bracketed by acceptable CCV analyte results.
ICB / CCB	Beginning of every analytical batch, immediately following the ICV. CCB is analyzed Immediately following each CCV.	< RL or if specified by project QAPP < ½ RL.	An ICB may be reanalyzed once. If the problem persists, correct the problem then re-analyze all samples for any analytes not bracketed by acceptable ICB analyte results.
LCS	One per sample preparation batch of up to 20 samples.	For 6010B and 6010C, LCS analyte recoveries must be within ± 20% of expected values. For 200.7, recoveries must be within ± 15%.	An LCS may be reanalyzed once in order to confirm unacceptable LCS analyte recoveries. If the problem persists, redigest all samples for any required analytes that have unacceptable LCS analyte recoveries. If the LCS analyte recoveries are biased high and the client sample recoveries are non-detect, the results may be reported with the appropriate flag.
MS/MSD	One per sample preparation batch of up to 20 samples (6010B/6010C) or one per every 10 or fewer samples (200.7).	75 - 125 % (6010B & 6010C) and 70 – 130% (200.7). Duplicate % RPD within ± 20%.	Report with the appropriate flag (M-Flag).

QC Check	Frequency	Acceptance Criteria	Corrective Action
DUP	One per sample preparation batch of up to 20 samples.	Duplicate % RPD within ± 20%.	Report with the appropriate flag (D-Flag).
CRDL/LLICV	Beginning of every analytical batch, immediately following the ICB. Method 6010C also requires analysis at the end of the analytical sequence.	Recoveries within ± 50% of true value for 200.7 and 6010B. For 6010C recoveries within ± 30%.	The CRDL may be reanalyzed once. If the problem persists, correct the problem then reanalyze all samples for affected analytes.
ICSA/AB	Beginning of every batch – Analyze ICSA and them AB.	ICSA/ICSAB spiked analytes within ± 10% of expected value for method 200.7 & 20% for methods 6010B/C. Non-spiked analytes within ± 2 times the RL.	The ICSA/ICSAB may be reanalyzed once. If the problem persists, correct the problem then re-analyze ICS and samples for affected analytes.
Dilution Test	One per prep batch if required by client.	If specified by project QAPP Five-fold dilution results within ± 10% of original measurement, original concentrations > 50x RL.	Client specified QAPP requirements.
Post-Digestion Spike Test	One per prep batch if required by client.	If specified by project QAPP. Recovery within ± 25%, expected recovery within 10-100x of RL. Recovery must be 80-120% for 6010C.	Client specified QAPP requirements.
MSA	If required by client.	No acceptance criteria. Refer to method 7000B section 9.10.	Document use of MSA in the final report.
LLCCV	After CCV following the CCB. Method 6010C also requires analysis at the end of the analytical sequence.	Recoveries within ± 30% of the true value for 6010C.	A LLCCV may be reanalyzed once. If the problem persists, correct the problem then re-analyze all samples for any analytes not bracketed by acceptable LLCCV analyte results.

15.17 MDLs/LODs will be determined as stated in SOP PGH-C-035.

15.17.1 The requirements that an analyst must meet prior to the commencement of work, include but are not limited to:

15.17.2 Reading and understanding the method and relevant SOPs,

15.17.3 Establishing an acceptable initial demonstration of capability (IDOC). For the IDOC an analyst must be able to calibrate and run four (4) Laboratory Control Samples (LCS). The resulting average of these 4

LCSs must be within ± 15 % of the true value for water and ± 20 % for soil with a standard deviation of less than 10.

15.18 Running an acceptable blind performance evaluation sample twice a year for water and soil.

15.19 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.20 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.21 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

16.2 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

16.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N. W., Washington, D.C. 20036, (202)872-4477

16.4 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel," available from the American Chemical Society.

17. References

17.1 T. D. Martin, C. A Brockhoff, J. T. Creed, and EMMC Methods Work Group – Method 200.7, Revision 4.4 (1994)

17.2 SW846 Method 6010B Inductively Coupled Plasma Atomic Emission Spectrometry Revision 2 December 1996.

17.3 SW846 Method 6010C Inductively Couple Plasma Atomic Emission Spectrometry Revision 3, February 2007.

17.4 Standard Methods, SM2340B, Hardness by Calculation, Approved by Standard Methods Committee, 1997.

17.5 Method 7000B, Flame Atomic Absorption Spectrophotometry, Section 9.10 Method of Standard Addition, Rev. 2, February 2007.

17.6 Help files located on the TJA 6500 computer.

17.7 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.8 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.9 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.10 SOP PGH-M-003, TCLP ZHE, current version.

17.11 SOP PGH-M-034, SPLP ZHE, current version.

17.12 SOP PGH-M-013, ICP Solid Digestion, current version.

17.13 SOP PGH-M-014, Microwave Digestion, current version.

17.14 SOP PGH-M-015, ICP Aqueous Digestion, current version.

17.15 SOP PGH-M-016, Percent Moisture, current version.

17.16 SOP PGH-C-026, Control Charts, current version.

17.17 SOP PGH-C-032, Support Equipment, current version.

17.18 SOP PGH-C-035, MDL-LOD, current version.

17.19 SOP PGH-C-037, Standard and Reagent Traceability, current version.

17.20 SOP PGH-Q-038, Laboratory Equipment, current version.

17.21 SOP S-ALL-Q-011, Audits, current version

17.22 SOP S-ALL-Q-012, Corrective Action, current version.

17.23 SOP S-ALL-Q-020, Training, current version,

17.24 SOP S-ALL-Q-028, Lab Track, current version.

17.25 Work Instruction, WI-PGH-Q-001, Marathon Analysis Guide, current version.

17.26 Work Instruction, WI-PGH-Q-002, NJ Data of Known Quality (DKQP) Guide.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

Table No. 1 – Typical Reporting Limits.

Table No. 2 – QC Sample Concentrations

Table No. 3. - Initial Calibration Curve Standard Concentrations.

Table No. 4. - Internal Standard referenced by the TJA 6500.

Table No. 5. – ICP Linear Ranges.

19. Method Modifications

19.1 This SOP does not deviate from the referenced methods.

20. Equipment Maintenance and Preventative Actions

20.1 The following maintenance may be performed as necessary. Document all maintenance actions performed in the maintenance log associated with the instrument.

20.1.1 The peristaltic pump tubing may become stretched, worn, or contaminated during normal operation. Replace the pump tubing as required.

20.1.2 The quartz torch may need periodic cleaning. The torch may be cleaned by submersion in a dilute acid solution (normally water 2% HNO_3 5% HCl) for approximately 15 minutes, rinsed with DI, and then completely dried before remounting.

20.1.3 The spray chamber may need periodic cleaning. The chamber may be cleaned by submersion in a dilute acid solution for approximately 15 minutes, rinsed with DI, and then dried before remounting.

20.1.4 The nebulizer may need periodic cleaning to prevent or remove salt buildup. The nebulizer may be cleaned utilizing the ELO-Flow nebulizer cleaner tool in conjunction with methanol. Flush the nebulizer two to three times with methanol, then flush with DI. Use an air source (compressed air, air can) to remove leftover moisture after cleaning.

20.1.5 The mixing coil kit may need to be periodically cleaned or replaced. Clean the mixing T by disconnecting from the intake lines, and then flushing with a dilute acid solution. The mixing lines may be cleaned by placing the internal standard and sample intake lines in a dilute acid solution while the instrument is on. (During warm-up suggested.) Replace lines that cannot be cleaned sufficiently.

21. Revisions

Document Number	Reason for Change	Date
PGH-M-008-12	1. See Archive copy for revision history	06Mar2014
PGH-M-008-13	1. Clarified section 8.4. 2. Changed Tin reporting limit for solid from 5 to 10 mg/kg. 3. Removed references to drinking water.	13Mar2014
PGH-M-008-14	1. Corrected several Section references. 2. Edited for grammar and spelling errors. 3. Document Reformatted. 4. Added SOP references.	24Jun2014
PGH-M-008-15	1. Corrected the hardness formula in section 13.2 for Hardness by Calculation, SM2340B. 2. Updated references including adding SM2340B. 3. Added table for linear ranges. 4. Clarified sections 14.14 and 14.15, post digestion and dilution test requirements.	04Mar2015
PGH-M-008-16	1. Updated the cover page, headers and footers for this revision 2. Section 8: Added Soil Hold Time requirement (8.5) 3. Section 11: Added Multi-point calibration section (11.2) 4. Section 15: Added Multi-point calibration section to table 5. Table 2: Added Multi-point ICV-CCV standards 5. Table 3: Added Multi-point calibration standards.	07Jul2015

Table 1 - Typical Aqueous and Solid Reporting Limits for the Trace ICP

Element	Typical Aqueous Reporting Limit (µg/L)	Typical Solid Reporting Limit (mg/Kg)
Aluminum	50	10
Antimony	6	0.6
Arsenic	5	0.5
Barium	10	2.0
Beryllium	1	0.2
Boron	50	5
Cadmium	3	0.3
Calcium	1000	200
Chromium	5	0.5
Cobalt	5	1.0
Copper	5	1.0
Iron	70	10
Lead	5	0.5
Lithium	50	10
Magnesium	200	50.0
Manganese	5	1.0
Molybdenum	20	2.0
Nickel	10	2.0
Phosphorus	50	10
Potassium	500	50
Sulfur	50	5
Selenium	8	0.8
Silicon	100	10
Silica	250	25
Silver	6	0.6
Sodium	1000	500
Strontium	5	1
Thallium	10	2
Tin	50	10
Titanium	5	1
Vanadium	5	1.0
Zinc	10	1.0
Zirconium	75	7.5

Table 2 - Concentrations of select Quality Control Solutions

Element	ICV (µg/L) (Single Point)	CCV (µg/L) (Single Point)	ICV (µg/L) (Multi Point)	CCV (µg/L) (Multi Point)	ICSA (µg/L)	ICSAB (µg/L)	LCS/MS (µg/L)
Aluminum	20000	10000	40000	20000	50000	50000	5000
Antimony	2000	1000	2000	2000			500
Arsenic	2000	1000	4000	2000			500
Barium	2000	1000	4000	2000		500	500
Beryllium	2000	1000	4000	2000		500	500
Boron	2000	1000	4000	2000			500
Cadmium	2000	1000	4000	2000		1000	500
Calcium	20000	10000	40000	20000	50000	50000	5000
Chromium	2000	1000	4000	2000		500	500
Cobalt	2000	1000	4000	2000		500	500
Copper	2000	1000	4000	2000		500	500
Iron	20000	10000	40000	20000	20000	20000	5000
Lead	2000	1000	4000	2000		1000	500
Lithium	2000	1000	4000	2000			500
Magnesium	20000	10000	40000	20000	50000	50000	5000
Manganese	2000	1000	4000	2000		500	500
Molybdenum	2000	1000	4000	2000			500
Nickel	2000	1000	4000	2000		1000	500
Phosphorus	2000	1000	4000	2000			500
Potassium	20000	10000	40000	20000			5000
Sulfur	20000	10000	40000	20000			500
Selenium	2000	1000	4000	2000			500
Silicon	10000	5000	20000	10000			2500
Silver	1000	500	2000	1000		1000	250
Sodium	20000	10000	40000	20000			5000
Strontium	2000	1000	4000	2000			500
Thallium	2000	1000	4000	2000			500
Tin	2000	1000	4000	2000			500
Titanium	2000	1000	4000	2000			500
Vanadium	2000	1000	4000	2000		500	500
Zinc	2000	1000	4000	2000		1000	500
Zirconium	2000	1000	4000	2000			500

Table 3 - Calibration Standard Concentrations (Single Point)

Element	Standard	Concentration (ug/L)	Element	Standard	Concentration (ug/L)
Ag	STD2A	1000	Na	STD2A	20000
Al	STD2A	20000	Ni	STD2A	2000
As	STD2A	2000	P	STD2A	2000
B	STD2A	2000	Pb	STD2A	2000
Ba	STD2A	2000	S	STD2A	20000
Be	STD2A	2000	Sb	STD2A	2000
Ca	STD2A	20000	Se	STD2A	2000
Cd	STD2A	2000	SI	STD2A	10000
Co	STD2A	2000	Sn	STD2A	2000
Cr	STD2A	2000	Sr	STD2A	2000
Cu	STD2A	2000	Ti	STD2A	2000
Fe	STD2A	20000	Tl	STD2A	2000
K	STD2A	20000	V	STD2A	2000
Li	STD2A	1000	Zn	STD2A	2000
Mg	STD2A	20000	Zr	STD2A	2000
Mn	STD2A	2000			
Mo	STD2A	2000			

Table 3 - Calibration Standard Concentrations (Multi-Point)

Element	Low Standard Concentration (ug/L)	Mid Standard Concentration (ug/L)	High Standard Concentration (ug/L)
Ag	500	1000	2000
Al	10000	20000	40000
As	1000	2000	4000
B	1000	2000	4000
Ba	1000	2000	4000
Be	1000	2000	4000
Ca	10000	20000	40000
Cd	1000	2000	4000
Co	1000	2000	4000
Cr	1000	2000	4000
Cu	1000	2000	4000
Fe	10000	20000	40000

Element	Low Standard Concentration (ug/L)	Mid Standard Concentration (ug/L)	High Standard Concentration (ug/L)
K	10000	20000	40000
Li	500	1000	2000
Mg	10000	20000	40000
Mn	1000	2000	4000
Mo	1000	2000	4000
Na	10000	20000	40000
Ni	1000	2000	4000
P	1000	2000	4000
Pb	1000	2000	4000
S	10000	20000	40000
Sb	1000	2000	4000
Se	1000	2000	4000
Si	5000	10000	20000
Sn	1000	2000	4000
Sr	1000	2000	4000
Ti	1000	2000	4000
Tl	1000	2000	4000
V	1000	2000	4000
Zn	1000	2000	4000
Zr	1000	2000	4000

Table 4 - Internal Standard referenced by the TJA 6500

Element	Internal Standard	Element	Internal Standard
Ag	Y	Na	Y
Al	Y	Ni	Y
As	Y	P	Y
B	Y	Pb	In
Ba	Y	S	Y
Be	Y	Sb	Y
Ca	Y	Se	Y
Cd	Y	Si	Y
Co	In	Sn	Y
Cr	Y	Sr	Y
Cu	Y	Ti	Y
Fe	Y	Tl	In
K	Y	V	Y
Li	Y	Zn	Y
Mg	Y	Zr	Y
Mn	Y		
Mo	In		

Table 5 - ICP Linear Dynamic Ranges (LDR)

Element	LDR ICP2 (ug/L)	LDR ICP3 (ug/L)
Ag (3280)	20000	5000
Al (3961)	1000000	500000
As (1890)	100000	75000
B (2089)	100000	100000
Ba (4554)	50000	50000
Be (3130)	20000	20000
Ca (3736)	1000000	1000000
Cd (2288)	20000	20000
Co (2286)	100000	50000
Cr (2677)	100000	100000
Cu (3247)	100000	100000
Fe (2611)	1000000	750000
K (7664)	50000	50000
Li (6707)	50000	100000
Mg (2790)	1000000	1000000
Mn (2576)	100000	100000
Mo (2020)	40000	50000
Na (8183)	1000000	1000000
Ni (2316)	100000	100000
P (1774)	100000	100000
Pb (2203)	100000	100000
Sb (2068)	100000	100000
Se (1960)	100000	100000
Si (2516)	250000	250000
Sn (1899)	100000	100000
Sr (4077)	20000	20000
Ti (3349)	100000	100000
Tl (1908)	100000	100000
V (2924)	100000	100000
Zn (2062)	100000	100000
Zr (3391)	40000	40000
S (1820)	500000	500000

STANDARD OPERATING PROCEDURE

Digestion of Solid Samples for Mercury Analysis
Methods: EPA 7471A & 7471B

SOP NUMBER:	PGH-M-012-8
REVIEW:	M. Kruth and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-M-012-7
REVIEW DATE:	Upon Procedural Change

APPROVALS

Marla L. Kruth	6/20/14
Assistant General Manager	Date
Maureen K. DeRubeis	7/13/14
Senior Quality Manager	Date
	7/10/14
Department Manager/Supervisor	Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

1. Purpose

1.1 This standard operating procedure (SOP) documents the steps to be followed for the preparation of solid or semi-solid samples for mercury analysis, by EPA 7471A and B.

2. Scope and Application

2.1 This procedure is used for the determination of total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludges.

2.2 This SOP is applicable to both the inorganic forms of mercury and the organic mercurials forms that may be present. Organo-mercury compounds will not respond to the cold vapor atomic absorption technique used in the analysis of mercury concentrations unless they are first broken down and converted to the mercuric ion.

2.3 Potassium permanganate may be used to oxidize many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.4 If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this procedure is not applicable for that matrix.

3. Summary of Method

3.1 A weighed portion of a sample is digested in a nitric acid and hydrochloric acid solution for 10 minutes at 95 ± 2°C in a hotblock.

3.2 The sample is then taken out of the hotblock and cooled.

3.3 Potassium permanganate ($KMnO_4$) is added to the sample and it is placed back in the hotblock for thirty (30) minutes to allow for oxidation and then allowed to cool.

3.4 The sample is then submitted for analysis. Samples are analyzed according to SOP PGH-M-017, Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy.

4. Interferences

4.1 Potassium permanganate is added to samples to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spike samples.

4.3 Samples high in chlorides require additional permanganate (as much as 25mL) since, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This maybe accomplished by using an excess of hydroxylamine hydrochloride reagent (25mL).

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

5.4 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

5.5 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be performed in a fume hood.

5.6 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 Batch: A set of no more than 20 samples, prepared and analyzed as a group that are associated with the same set of QC samples.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Non-aqueous samples shall be refrigerated at ≤6ºC.

8.2 Both plastic and glass containers are suitable for sample collection.

8.3 Samples must be prepared within 28 days of collection and analyzed as soon as possible.

8.4 Because of the sensitivity of the analytical procedure and the presence of mercury in the laboratory environment, extreme care must be taken to avoid extraneous contamination. Sampling devices, sample containers, and plastic items must be determined to be free of mercury, and samples must not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

9. Equipment and Supplies

9.1 Environmental Express hotblock. or equivalent

9.2 Disposable Polypropylene Digestion Vessels (PDV) with caps, 50mL and 100mL.

9.3 Environmental Express hotblock rack(s), or equivalent.

9.4 Thermometers- Traceable to NIST calibration and capable of measuring 95 ± 3°C.

9.5 Assorted glass Class A and calibrated air displacement pipettes.

9.6 Volumetric flasks and graduated cylinders, Class A, glass.

9.7 Wooden tongue depressors Fisher Scientific or equivalent.

9.8 Analytical Balance: capable of weighing 0.01g, or equivalent.

9.9 Polypropylene beads, or equivalent.

10. Reagents and Standards

10.1 Reagent (Millipore) Water, ASTM Type II (DI water).

10.2 Concentrated Nitric Acid (HNO_3) - Fisher Scientific TraceGrade® for mercury determination, or equivalent.

10.3 Concentrated Hydrochloric Acid (HCl) - Fisher Scientific TraceGrade® for mercury determination, or equivalent.

10.4 Potassium Permanganate($KMnO_4$)- Fisher Scientific Suitable for mercury determination, or equivalent.

10.5 1,000µg/mL Mercury Stock Solutions (2 Sources) from Inorganic Ventures and High Purity Standards, or Equivalent.

10.6 Mercury Standards

10.6.1 Add approximately 50mL DI water and 2mL concentrated HNO_3 to a 100mL Class A volumetric flask. Pipette 100µl of the 1000µg/mL mercury stock solution (Source 1) into the flask and dilute to volume with DI water.

10.6.1.1 The final concentration of this solution is 1µg/mL and is labeled as Intermediate Source 1.

10.6.2 Add approximately 50mL DI water to a second 100mL Class A volumetric flask. Pipette 25mL of the solution from the flask labeled Intermediate Source 1 into the second flask and dilute to volume with DI water.

10.6.2.1 The final concentration of this solution is 0.25µg/ml and is labeled as Source 1.

10.6.2.2 This solution is used to prepare the working calibration standards.

10.6.3 Prepare another 1000µg\mL Mercury Stock Solution from a second source (Source 2) and label the flasks Intermediate Source 2 and Source 2 on the respective flasks.

10.6.3.1 This solution will be used to prepare the ICV and LCS samples.

10.7 Potassium Permanganate ($kMnO_4$), 5% Solution - Dissolve 5g of potassium permanganate in 100mL of reagent water.

10.8 Aqua regia - A solution made up of at a ratio of three parts concentrated HCl and one part concentrated HNO_3. (3:1 HCl:HNO_3)

10.9 Hydroxylamine hydrochloride solution; Dissolve 12g hydroxylamine hydrochloride in DI water and dilute to 100mL in a volumetric flask.

10.10 Refer to the appropriate Certificate of Analysis located in the preparation area for relevant information regarding purification, storage conditions, and expiration dates for the referenced standards, chemicals, and reagents.

10.11 Record the identifications of all standards and solutions in the metals standard logbook.

11. Calibration

11.1 The temperature of the hotblock will be calibrated against a thermometer that is NIST traceable to verify the temperature of the solution in the PDV.

11.2 The analytical balance calibration must be confirmed daily, prior to use.

12. Procedure

12.1 Identify the solid samples that will be prepared for mercury analysis and retrieve them from sample storage.

12.1.1 If the sample is from a client that requires an internal chain of custody, fill out the internal chain of custody logbook for the metals department.

12.2 Turn on the hotblock and let it warm up to 95 ± 3°C.

12.2.1 The actual temperature of the hotblock is measured with a NIST thermometer that is suspended in a PDV filled with water.

12.2.1.1 Adjust the temperature of the hotblock until the water in the PDV containing the NIST thermometer measures 95 ± 3°C.

12.3 Record the sample information in the solid mercury digestion logbook. Complete all of the requested information. (See Attachment No. 2).

12.4 Write the project and sample identification numbers on a PDV for each sample.

12.5 Weigh 0.6 ±0.05g of untreated sample into the corresponding PDV.

12.6 Add 25mLs DI water to each PDV.

12.6.1 For the duplicate (DUP) sample, write the same project and sample identification number on two PDVs.

12.6.1.1 On one of the PDVs add the letters DUP after the sample identification.

12.6.1.2 Weigh 0.6 ±0.05g untreated sample into each PDV.

12.6.2 For each matrix spike (MS) and matrix spike duplicate (MSD) sample that is prepared, write the same project and sample identification number on three PDVs.

12.6.2.1 On one of the PDVs, add the letters MS after the sample identification.

12.6.2.2 On another PDV, add the letters MSD after the sample identification.

12.6.2.3 Weigh 0.6 ± 0.05g untreated sample into each PDV.

12.6.2.3.1 Pipette 250µL of Source 1 into the sample labeled as a MS and MSD.

12.6.2.3.2 This is the same standard source used for the working calibration standards.

12.6.2.3.3 The spike concentration of the MS and MSD sample is 2.5µg/L.

12.7 Using the Source 1 standard, prepare a set of mercury working calibration standards with every batch of samples.

12.7.1 Label six PDVs as Blank, Std 1, Std 2, Std 3, Std 4, and Std 5.

12.7.2 Add the following to the labeled PDVs;

Blank: 25mL reagent water

Std 1: Pipette 20µLof the Source 1 standard into a PDV containing 10mL of DI water. Dilute to 25mL with DI water for a final concentration of 0.2µg/L.

Std 2: Pipette 50µL of the Source 1 standard into a PDV containing 10mL of DI water. Dilute to 25mL with DI water for a final concentration of 0.5µg/L.

Std 3: Pipette 100µLof the Source 1 standard into a PDV containing 10mL of DI water. Dilute to 25mL with DI water for a final concentration of 1.0µg/L.

Std 4: Pipette 500µLof the Source 1 standard into a PDV containing 10mL of DI water. Dilute to 25mL with DI water for a final concentration of 5.0µg/L.

Std 5: Pipette 1000µLof the Source 1 standard into a PDV containing 10mL of DI water. Dilute to 25mLs with DI water for a final concentration of 10.0µg/L.

12.8 Prepare an Initial Calibration Verification (ICV) standard with every batch of samples.

12.8.1 Label a PDV as ICV

12.8.1.1 Pipette 100µLof the Source 2 standard into the PDV to which 10mLs of DI water has been added.

12.8.1.2 Dilute to 25mLs with DI water for a final concentration of 1µg/L.

12.9 Prepare a Laboratory Control Sample (LCS) sample with every batch of samples.

12.9.1 Label a PDV as LCS

12.9.1.1 If a certified solid mercury standard is available, weigh an amount that would yield a final concentration that is within the linear range of the working calibration standards. Bring up to a volume of 25mL with DI water.

12.9.1.2 If a certified solid mercury standard is not available, weigh 0.6g polypropylene beads into the PDV, pipette 100µL of the Source 2 standard into the PDV and dilute to 25mL with DI water for a final concentration of 1µg/L.

12.10 Prepare a Preparation Blank (PB) sample with every batch

12.10.1 Label a PDV as PB

12.10.2 Weigh 0.6g polypropylene beads and add 25mL of DI ater to the PDV labeled as PB

12.11 The CCV standard uses working calibration standard 4 which is at a concentration of 5.0µg/L.

12.12 Place the samples and standards in a plastic hotblock rack and place them in a hood.

12.13 Add 1.25mL of aqua regia to each PDV.

12.14 Lay a cap loosely on top of each PDV.

12.15 Place the rack containing the PDVs into the hotblock for 10 minutes to digest the samples for method 7471A or for 2 minutes to digest the samples for method 7471B.

12.16 At the end of 10 minutes for the samples for method 7471A or the 2 minutes for the samples for method 7471B, remove the rack from the hotblock and allow the PDV's to cool.

12.17 Remove the caps and add 3mL potassium permanganate ($KMnO_4$) to each PDV.

12.18 Securely place the cap on the PDVs and shake each sample and standard to thoroughly mix the contents.

12.18.1 If the purple color of the $KMnO_4$ disappears within 15 minutes of its addition to any sample, add additional $KMnO_4$ until the purple color persists for at least 15 minutes

12.19 Remove the cap, and loosely place it back on of the PDV's.

12.19.1 Do not proceed with the digestion step with the caps securely in place.

12.20 Place the rack back into the hotblock for 30 minutes.

12.21 At the end of 30 minutes, remove the rack from the hotblock and allow the PDVs to cool to room temperature.

12.22 Submit the samples and a copy of the mercury preparation logbook page(s) to the instrument lab for analysis.

13. Calculations

13.1 Not applicable.

14. Quality Control

14.1 At a minimum each batch of samples shall have at a minimum the following QC samples:

14.1.1 One Method Blank.

14.1.2 One Laboratory Control Sample.

14.1.3 One Matrix Spike and one Matrix Spike Duplicate.

14.1.4 One Duplicate Sample.

14.1.5 One Initial Calibration Verification Standard.

14.1.6 One set of Calibration Standards.

14.2 Corrective Actions for Out-Of-Control Data

14.2.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.2.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.2.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and the results noted in the final report.

14.2.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the

MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.2.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.2.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.2.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.2.5.2 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their reporting limit, and duplicate precision meets the acceptance criteria.

14.2.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 An analyst shall not prepare samples by this method without supervision until they have completed the following requirements:

15.1.1 Read and understand this SOP and referenced methods.

15.1.2 Complete an initial demonstration of capability (IDOC).

15.1.2.1 An IDOC consists of preparing four (4) LCS samples that when analyzed meet the required acceptance criteria.

15.2 If the thermostat of the hotblock will not maintain temperature or cannot be calibrated against the NIST traceable thermometer, discontinue using it. Tag the hotblock as “out of service” and notify the Quality Control Department and the Department Manager/Supervisor.

15.3 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.4 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.5 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical’s Chemical Hygiene Plan and in the SDSs.

16.2 All chemicals, reagents, and solutions should be used with proper ventilation.

16.3 Keep the volume of the solutions to the smallest amount needed to accomplish the task at hand. This will minimize the amount of solution spilled if the PDV or flask is accidentally knocked over or broken.

16.4 Use funnels when pouring solutions to avoid splashing or spills.

16.5 Where possible, dispense acids and solutions in bottles with a bottle top dispenser to avoid splashing or spills.

16.6 All solutions, chemicals and reagents used or generated during this procedure must be disposed of in compliance with all regulations and requirements and the laboratory's waste handling and disposal policy.

17. References

17.1 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.2 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.3 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.4 Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods. Third Edition as Amended Through Update III, Method 7471A.

17.5 Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, Third Edition, Final Update IV, Method 7471B, Mercury in Solid or Semisolid Waste, Revision 2, Feb 2007.

17.6 version.

17.7 SOP PGH-M-017, Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

Figure #1 : Flowchart for the preparation of mercury in an solid or semi-solid matrix.

Table #1 : Potential problems that may occur with the process of this SOP and corrective actions.

Attachment No. 1: Mercury Digestion Logbook – Solid (Example)

19. Revisions

Document Number	Reason for Change	Date
PGH-M-012-6	1. Updated Section 12.9.1.2: If a certified solid mercury standard is not available, weigh 0.6g of polypropylene beads into the PDV, pipette 100µls of the Source 2 standard into the PDV and dilute to 25mL with DI water for a final concentration of 1µg/L.	11Oct2013
PGH-M-012-7	1. Added to Section 3: Samples are analyzed according to SOP PGH-M-017, Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy.	06Mar2014
PGH-M-012-8	1. Changed all references of ppb to µg/L. 2. Changed Section 20 heading to Method Modifications. 3. General editing for grammar and punctuation. 4. Document Reformatted.	20Jun2014

20. Method Modifications

20.1 The Environmental Express hotblock and Polyethylene Digestion Vessels are used (with equivalent reductions in reagents) to digest the samples in place of the hotplate and BOD bottles listed in the method.

20.2 Instead of adding 100mL of DI to the untreated sample in the BOD bottles, 25mL of DI is added to the untreated sample in the PDVs.

20.3 Difference in reagent volumes:

20.3.1 1.25 mL of aqua regia is used instead of 5.0mL.

20.3.2 3.00 mL of $KMnO_4$ is used instead of 15mL.

Figure #1 – Digestion Flowchart

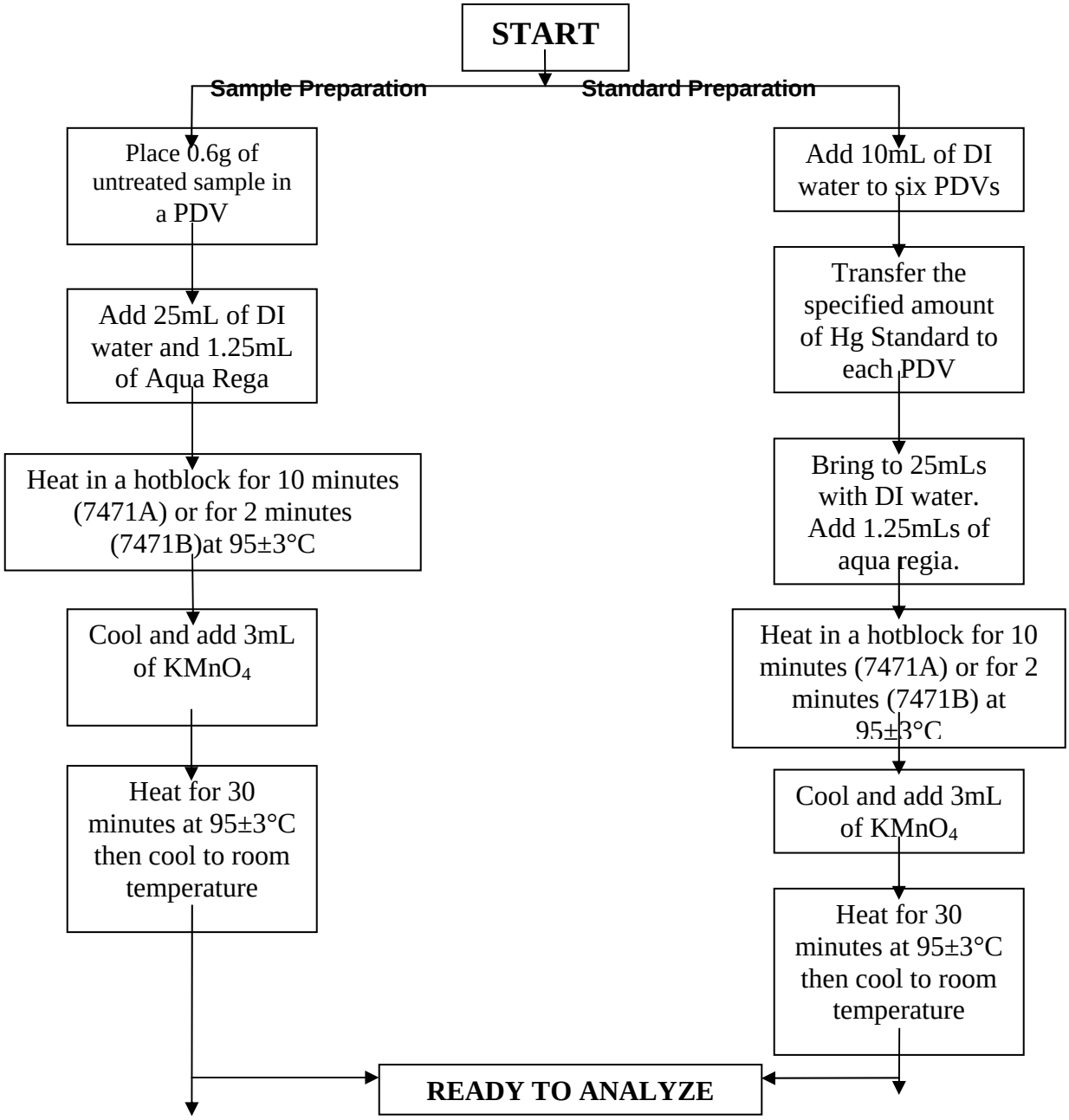


Table #1 - Corrective Action/Preventative Actions

Active SOP	Potential Problems	Corrective Actions
Using hotblock and PDVs	Hotblock needs repaired or low supply of PDVs	Use water bath and BOD Bottles.
Adding: Add: 1.25mLs aqua regia, 3.00mLs $KMnO_4$ per 25mL Aliquot.	Hotblock needs repaired or low supply of PDVs	Add: 5.0mLs aqua regia, 15mLs of $KMnO_4$ per 100mL aliquot.

Attachment No. 1 - Mercury Digestion Logbook – Solid (Example)

Pace Analytical Services, Inc.-PGH

Mercury Metals Digestion Sheet (Solid)

Doc.#:M002 Rev.1
Batch#:_____
Run#:_____
Analyst:_____
Prep Date:_____

Hotblock Temp: _____
HNO3 ID#:_____
HCl ID#:_____
H-Hydrochloride ID#:_____
S. Chloride ID#:_____
Digestion Container Lot#_____

Standard/Spike ID#:_____
ICV ID#:_____
Solid QC (LCS) ID#:_____
KMnO4 ID#:_____

Stds:Blank: 0.0ug\L; **Std 1:** 0.2ug\L; **Std 2:** 0.5ug\L; **Std3:** 1.0ug\L; **Std 4:** 5.0ug\L; **Std 5:** 10.0ug\L

Project	Sample ID	Initial Weight (g)	Final Volume (ml)	Comments
	PB ( )			QC-
	LCS ( )			
	DUP			
	MS			

STANDARD OPERATING PROCEDURE

Digestion of Aqueous Samples for Mercury Analysis
Methods: 245.1 and 7470A

SOP NUMBER:	PGH-M-011-6
REVIEW:	Tim Harrison and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-M-011-5
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	6/2/14 Date
Senior Quality Manager	7/13/14 Date
Department Manager/Supervisor	7/11/14 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This standard operating procedure (SOP) documents the steps to be followed for the preparation of aqueous samples for mercury analysis per methods 245.1, rev.3.0 and 7470A.

2. Scope and Application

2.1 This procedure describes the process to be used to determine the concentration of mercury in surface, saline and ground waters, domestic and industrial waste waters. This procedure can also used to determine the concentration of mercury in mobility-procedure extracts (TCLP & SPLP) (for method 7470A only).

2.2 This SOP is applicable to both the inorganic forms of mercury and the organic mercurial forms that may be present. Organo-mercury compounds will not respond to the cold vapor atomic absorption technique used in the analysis of mercury concentrations unless they are first broken down and converted to the mercuric ion.

2.3 Potassium permanganate may be used to oxidize many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.4 If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this procedure is not applicable for that matrix.

2.5 The typical calibration range for this procedure is 0.2 to 10µg/L, but it can be extended above or below this range by increasing or decreasing the sample size.

3. Summary of Method

3.1 A 25mL aliquot of a well mixed aqueous sample is poured into a polypropylene digestion vessel and the following reagents are added: sulfuric acid, nitric acid, potassium permanganate, and potassium persulfate. The solution is heated in the hot-block digester for two hours and then allowed to cool. The sample is then submitted for analysis.

3.2 Samples are analyzed according to SOP PGH-M-017, Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy.

4. Interferences

4.1 Potassium permanganate is added to samples to eliminate possible interference from sulfide. Concentrations as high as 20mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10mg/L had no effect on recovery of mercury from spike samples.

4.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25mL) since, during the oxidation step, chlorides are converted to free chlorine, which also absorbs light at 253.7nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This maybe accomplished by using an excess of hydroxylamine hydrochloride reagent (25mL).

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

5.4 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory fume hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

5.5 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be performed in a fume hood.

5.6 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 Batch - A set of no more than 20 samples, prepared and analyzed as a group that is associated with the same QC samples.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Because of the sensitivity of the analytical procedure and the presence of mercury in the laboratory environment, extreme care must be taken to avoid extraneous contamination. Sampling devices, sample containers, and plastic items must be determined to be free of mercury; and the samples must not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

8.2 Preservation of Samples for Mercury Analysis

8.2.1 For the analysis of total mercury in aqueous samples, samples are not filtered, but are acidified with 1:1 nitric acid to pH<2 (normally, 3mL of 1:1 nitric acid per liter of sample is sufficient for most ambient water samples).

8.2.2 For the analysis of dissolved mercury in aqueous samples, the sample must be filtered through a 0.45µm filter paper and then preserved with 1:1 nitric acid to a pH<2.

8.2.3 Preservation may be performed at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, it is recommended that the samples be returned to the laboratory as soon as possible after collection and acid preserved upon receipt in the laboratory. Following acidification, the sample must be mixed and held for 24 hours. The sample is then verified to be at a pH<2 prior to the withdrawal of an aliquot for preparation.

8.2.3.1 If the sample pH is verified to be >2, then more nitric acid must be added to the sample and it must be held for an additional 24 hours and re-verified to be at a pH<2.

8.2.4 The preserved sample must be analyzed within 28 days of collection.

8.3 A field blank should be prepared in the field and submitted for analysis as required by the data user using the same container type and acid strength as used for the sample collection.

9. Equipment and Supplies

9.1 Environmental Express hotblock, or equivalent.

9.2 Disposable Polypropylene Digestion Vessels (PDV) with caps (50mL and 100mL).

9.3 Environmental Express hotblock rack(s), or equivalent.

9.4 Thermometers- Traceable to NIST calibration and capable of measuring 95±2°C.

9.5 Assorted glass Class A and calibrated air displacement pipettes.

9.6 Volumetric flasks and graduated cylinders, Class A, glass.

9.7 Environmental Express Flipmate® Filters, or equivalent.

10. Reagents and Standards

10.1 Reagent (Millipore) Water; Type II.

10.2 Concentrated Nitric Acid (HNO_3) - Fisher Scientific Trace Metal Grade, or equivalent.

10.3 Concentrated Sulfuric Acid (H_2SO_4) - Fisher Scientific Trace Metal Grade, or equivalent.

10.4 Potassium Persulfate ($K_2S_2O_8$) - Fisher Scientific, Suitable for Mercury Determination, or equivalent.

10.5 Potassium Permanganate ($KMnO_4$) - Fisher Scientific, Suitable for Mercury Determination or equivalent.

10.6 1,000µg/mL Mercury Stock Solutions (2 Sources) from Spex and CPI, or Equivalent.

10.7 Hydroxylamine Hydrochloride Solution: Dissolve 12g hydroxylamine hydrochloride in DI water and dilute to the mark in a 100mL volumetric flask.

10.8 Mercury Standards

10.8.1 Add approximately 50mL of reagent water and 2mL of concentrated HNO_3 to a 100mL Class A volumetric flask. Pipette 100uL of the 1000µg/mL mercury stock solution (Source 1) into the flask and dilute to volume with reagent water.

10.8.1.1 The final concentration of this solution is 1ug/mL and is labeled as Intermediate Source 1.

10.8.2 Add approximately 50mL of reagent water to a second 100mL Class A volumetric flask. Pipette 25mL of the solution from the flask labeled Intermediate Source 1 into the second flask and dilute to volume with reagent water.

10.8.2.1 The final concentration of this solution is 0.25ug/mL and is labeled as Source 1.

10.8.2.2 This solution is used to prepare the working calibration standards.

10.8.3 Prepare another 1000µg\mL Mercury Stock Solution from a second source (Source 2) by repeating steps 11.7.1 and 11.7.2 and label the flasks Intermediate Source 2 and Source 2 on the respective flasks.

10.8.3.1 This solution will be used to prepare the ICV and LCS standards.

10.9 Potassium Persulfate (5% Solution) - Dissolve 5g of Potassium Persulfate in 100mL of reagent water.

10.10 Potassium Permanganate (5% Solution) - Dissolve 5g of Potassium Permanganate in 100mL of reagent water.

10.11 Refer to the appropriate Certificate of Analysis located in the preparation area for relevant information regarding purification, storage conditions, and expiration dates for the referenced standards, chemicals, and reagents.

10.12 Record the identifications of all standards and solutions in the metals standard logbook.

11. Calibration

11.1 The temperature of the hotblock will be calibrated against a thermometer that is NIST traceable to verify the temperature of the solution in the PDV.

11.2 Air displacement pipettes must be calibrated quarterly.

12. Procedure

12.1 Turn on the hotblock and let it warm up to the set temperature of 110.0°C, which is displayed on the digital LED.

12.1.1 The actual temperature of the hotblock is measured with a NIST thermometer that is suspended in a PDV filled with water.

12.1.2 Adjust the temperature of the hotblock until the water in the PDV containing the NIST thermometer measures 95°C±2°C and record the digital display reading.

12.2 If the sample is from a client that requires an internal chain of custody, fill out the internal chain of custody logbook for the Metals Department.

12.3 Record the sample information in the aqueous mercury digestion logbook. Complete all of the requested information. (See Attachment No. 2).

12.4 Write the project and sample identification numbers on a PDV for each sample.

12.5 Shake each sample well and immediately pour a 25mL aliquot into the corresponding PDV.

12.5.1 For duplicate (DUP) samples, write the same project and sample identification number on two PDVs.

12.5.1.1 On one of the PDVs add the letters DUP after the sample identification.

12.5.1.2 Shake the sample well and immediately pour a 25mL aliquot of the sample into each PDV.

12.5.2 For matrix spike (MS) samples, write the same project and sample identification number on two PDVs.

12.5.2.1 On one of the PDVs add the letters “MS” after the sample identification.

12.5.2.2 Shake the sample well and immediately pour a 25mL aliquot of the sample into each PDV.

12.5.2.2.1 Pipette 250µL of Source 1 into each sample that is labeled as a MS.

12.5.2.2.2 This is the same standard source used for the working calibration standard.

12.5.2.2.3 The spiked concentration of each MS samples is 2.5µg/L.

12.6 Using the Source 1 standard, prepare a set of mercury working calibration standards with every batch of samples.

12.6.1 Label six PDVs as Blank, Std 1, Std 2, Std 3, Std 4, and Std 5. Place the batch letter on each PDV to link the standards to the batch.

12.6.2 Add the following to the labeled PDVs;

Blank: 25mLs of reagent water

Std 1: Pipette 20µL of the Source 1 standard into a PDV containing 10mL of reagent water. Dilute to 25mL with reagent water for a final concentration of 0.2µg/L.

Std 2: Pipette 50µL of the Source 1 standard into a PDV containing 10mL of reagent water. Dilute to 25mL with reagent water for a final concentration of 0.5µg/L.

Std 3: Pipette 100µL of the Source 1 standard into a PDV containing 10mL of reagent water. Dilute to 25mL with reagent water for a final concentration of 1.0µg/L.

Std 4: Pipette 500µL of the Source 1 standard into a PDV containing 10mL of reagent water. Dilute to 25mL with reagent water for a final concentration of 5.0µg/L.

Std 5: Pipette 1000µL of the Source 1 standard into a PDV containing 10mL of reagent water. Dilute to 25mL with reagent water for a final concentration of 10.0µg/L.

12.7 Prepare an ICV standard with every batch of samples.

12.7.1 Label a PDV as “ICV”

12.7.1.1 Pipette 100µL of the Source 2 standard into the PDV containing 10mL of reagent water.

12.7.1.2 Dilute to 25mL with reagent water for a final concentration of 1µ/L.

12.8 Prepare a LCS sample with every batch of samples

12.8.1 Label a PDV as LCS

12.8.1.1 Pipette 100µL of the Source 2 standard, (the same source as used for the ICV standard), into the PDV containing 10mL of reagent water, dilute to 25mL with reagent water for a final concentration of 1µg/L.

12.8.1.2 If the sample is for dissolved mercury, a filtered LCS must be digested.

12.8.1.3 Fill a clean 250mL bottle with 100mL of reagent water, pipette 400µL of Source 2 standard into the regeant water, add 2mL of HNO_3 to the solution and filter.

12.8.1.4 Label the clean 250mL bottle with the lot number of the flipmate filter, the reagent number of the HNO_3, the standard identification number, and the date.

12.8.1.5 Pour 25mL of the solution into a PDV labeled as the LCS for any dissolved samples being digested.

12.9 Prepare a preparation blank (PB) sample with every batch

12.9.1 Label a PDV as PB

12.9.2 Add 25mL of reagent water to the PDV labeled as PB

12.9.2.1 If the sample is for dissolved mercury, a filtered PB must be digested.

12.9.3 Fill a clean 500mL bottle with reagent water and filter the reagent water.

12.9.3.1 Add 2mL of concentrated HNO_3 to the reagent water.

12.9.3.2 Label the clean 500mL bottle with the lot number of the flipmate filter, the reagent number of the HNO_3, and the date.

12.9.3.3 Label the clean 500mL bottle with the lot number of the flipmate filter, the reagent number of the HNO_3, and the date.

12.10 The CCV Standard uses working calibration standard 4 from Section 15.6.1, which is at a concentration of 5.0µg/L..

12.11 Place all samples and standards in a hood and add the following reagents to each PDV:

12.11.1 1.25mL concentrated H_2SO_4

12.11.2 0.625mL concentrated HNO_3

12.11.3 3.75mL $KMnO_4$

12.12 Place the cap securely on each PDV and shake each sample and standard to thoroughly mix the contents.

12.12.1 If the purple color of the $KMnO_4$ disappears within 15 minutes of its addition to any sample, add an additional 3.75mL of $KMnO_4$ until the purple color persists for at least 15 minutes.

12.12.2 If additional $KMnO_4$ is added to any sample then equal amounts of $KMnO_4$ must be added to all samples, standards, and blanks

12.13 Remove the cap from each PDV and add 2mL of $K_2S_2O_8$.

12.14 Place the cap securely on each PDV and shake each sample and standard to thoroughly mix the contents.

12.15 Place the PDV's in the plastic hotblock rack and remove each cap and set it loosely on top of the PDV.

12.15.1 Do not proceed with the digestion step with the caps securely in place.

12.16 Place the racks containing the PDVs into the hotblock and heat the samples and standards at 95±2°C for 2 hours.

12.17 After 2 hours, remove the sample and standards from the hotblock and allow them cool to room temperature.

12.18 Submit the samples and standards and a copy of the mercury preparation logbook page(s) to the instrument lab for analysis.

13. Calculations

13.1 Not applicable.

14. Quality Control

14.1 Each batch of samples (20 or fewer) shall have at a minimum the following QC samples;

14.1.1 One Prep Blank (PB).

14.1.2 One LCS (called lab fortified blank in method 245.1).

14.1.3 Two Matrix Spikes (MS) (one MS per 10 samples) (called lab fortified matrix in method 245.1).

14.1.3.1 Prepared using two different samples.

14.1.4 Two Duplicate Samples (DUP) (one dup per 10 samples).

14.1.4.1 Prepared using two different samples.

14.1.5 One ICV.

14.1.6 One set of Calibration Standards.

14.2 Corrective Actions for Out-Of-Control Data

14.2.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.2.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.2.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and the results noted in the final report.

14.2.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.2.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.2.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.2.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.2.5.2 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their the reporting limit, and duplicate precision meets the acceptance criteria.

14.2.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 An analyst shall not prepare samples by this method without supervision until they have completed the following requirements:

15.1.1 Read and understand this SOP and referenced methods.

15.1.2 Complete an initial demonstration of capability (IDOC).

15.1.2.1 An IDOC consists of preparing four (4) LCS samples that when analyzed meet the required acceptance criteria.

15.2 If the thermostat of the hotblock will not maintain temperature or cannot be calibrated against the NIST traceable thermometer, discontinue using it. Tag the hotblock as “out of service” and notify the quality control department and the department supervisor.

15.3 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.4 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.5 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

16.2 All chemicals, reagents, and solutions should be used in a hood.

16.3 Keep the volume of the solutions to the smallest amount needed to accomplish the task at hand. This will minimize the amount of solution spilled if the PDV or flask is accidentally knocked over or broken.

16.4 Use funnels when pouring solutions to avoid splashing or spills.

16.5 Where possible, dispense acids and solutions in bottles with a bottle top dispenser to avoid splashing or spills.

16.6 All solutions, chemicals and reagents used or generated during this procedure must be disposed of in compliance with all regulations and requirements and the laboratory’s waste handling and disposal policy.

17. References

17.1 Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods. Third Edition as Amended Through Update III, Method 7470A.

17.2 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 March 1979, Third Edition, Method 245.1.

17.3 Methods for the Determination of Metals in Environmental Samples, EPA-600/R-94/111 May 1994 Supplement 1. Method 245.1, Revision 3.0, EMMC Version.

17.4 SOP PGH-M-017, Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy.

17.5 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.6 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.7 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

Figure #1 : Flowchart for the preparation of mercury in an aqueous matrix.

Table #1 : Potential problems that may occur with the process of this SOP and corrective actions.

Attachment No. 1: Mercury Digestion Logbook – Aqueous (Example)

19. Revisions

Document Number	Reason for Change	Date
PGH-M-011-5	1. Removed references to drinking water.	03/13/14
PGH-M-011-6	1. Cover and Section 1.1: clarified method references. 2. Section 8.2.3: changed 16 to 24 hours. 3. General: made editorial corrections. 4. Document Reformatted.	02Jun2014

20. Method Deviations

20.1 The Environmental Express hotblock and Polyethylene Digestion Vessels are used (with equivalent reductions in reagents) to digest the samples in place of the hotplate and BOD bottles listed in the method.

20.1.1 Instead of using an aliquot of 100mL in the BOD bottles, an aliquot of 25mL is used in the PDVs.

20.2 Differences in reagent volumes: (adjusted for use in the PDVs)

20.2.1 1.25mL of H_2SO_4 is used instead of 5.0mL.

20.2.2 0.625mL of HNO_3 is used instead of 2.5mL.

20.2.3 3.75mL of $KMnO_4$ is used instead of 15mL.

20.2.4 2.0mL of $K_2S_2O_8$ is used instead of 8mL.

20.3 Method 245.1 Section 11.2.2 states prepare calibration standards without heating. The laboratory treats samples and standards the same by digesting standards and samples.

Figure #1 – Digestion Flowchart

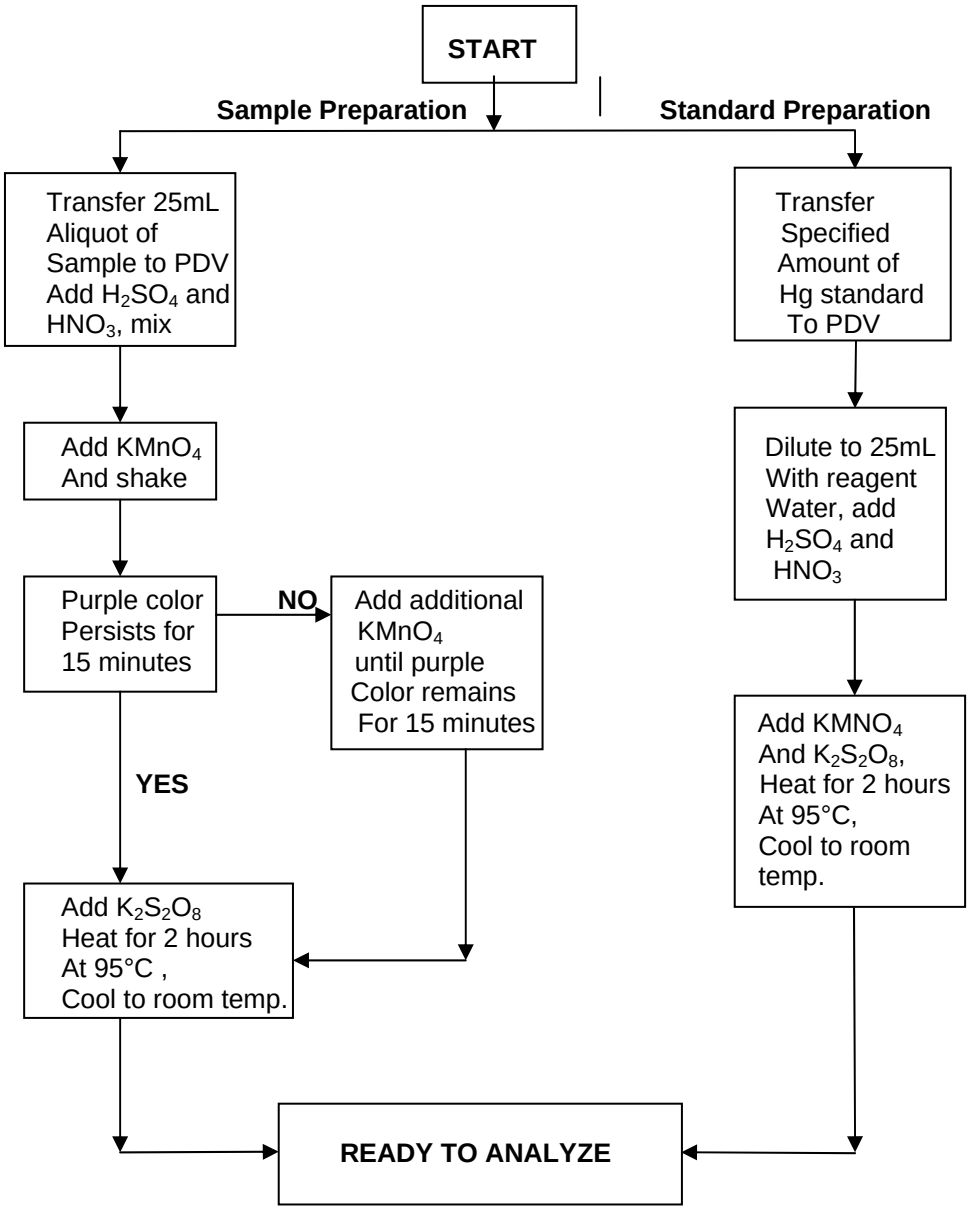


Table #1 - Corrective Actions/Preventative Actions

Active SOP	Potential Problems	Corrective Actions
Using hotblock and PDVs BOD	Hotblock needs repaired or low Supply of PDVs	Use water bath and bottles
Adding: 1.25mL H_2SO_4 0.625mL HNO_3 3.75mL $KMnO_4$ 2mL $K_2S_2O_8$ -per 25mL aliquot	Hotblock needs to be repaired or low Supply of PDVs	Add: 5mL H_2SO_4 2.5mL HNO_3 15mL $KMnO_4$ 8mL $K_2S_2O_8$ -per 100mL aliquot

Attachment No. 1 - Mercury Digestion Logbook – Aqueous (Example)

Pace Analytical Services, Inc.-PGH

Mercury Metals Digestion Sheet (Liquid)

Doc.#: M001Rev.1 Hotblock Temp: _____ °C Standard/Spike ID#: _____

Batch#: _____ HNO3 ID#: _____ ICV/LCS ID#: _____

Run#: _____ H2SO4 ID#: _____ H-Hydrochloride ID#: _____

Analyst: _____ KMnO4 ID#: _____ S. Chloride ID#: _____

Prep Date: _____ K. Persulfate ID#: _____ Time On: _____ Time OFF: _____

Digestion Container Lot# _____

Stds:Blank: 0.0ug\L; **Std 1:** 0.2ug\L; **Std 2:** 0.5ug\L; **Std3:** 1.0ug\L; **Std 4:** 5.0ug\L; **Std 5:** 10.0ug\L

Project	Sample ID	Initial Volume (ml)	Final Volume (ml)	Comments
	PB ( )			QC-
	LCS ( )			
	DUP			
	MS			
	DUP			
	MS			

STANDARD OPERATING PROCEDURE

Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy
(Cetac)
Methods: EPA 245.1, 7470A, 7471A and 7471B

SOP NUMBER:	PGH-M-017-5
REVIEW:	Tim Harrison and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-M-017-4
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	6/2/14 Date
Senior Quality Manager	7/13/14 Date
Department Manager/Supervisor	7/11/14 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This Standard Operating Procedure (SOP) documents the procedures used to determine total mercury in liquid samples based on EPA Method 245.1, rev.3.0 and SW-846 Method 7470A. It will also be used to determine total mercury in solid samples based on SW-846 Method 7471A and 7471B.

2. Scope and Application

2.1 This is a cold-vapor atomic absorption procedure used for determining the concentration of mercury in mobility-procedure extracts (method 7470A only), aqueous wastes, and ground waters; it is also used for analyzing certain solid and sludge-type wastes. All samples must be subjected to an appropriate dissolution step prior to analysis.

3. Summary of Method

3.1 Prior to analysis, the samples must be prepared according to the mercury digestion procedures for the preparation of aqueous samples (SOP PGH-M-011) or solid samples (SOP PGH-M-012).

3.2 This procedure uses a cold-vapor atomic absorption technique which is based on the absorption of light at the 253.7nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. The absorbance (peak height) is measured as a function of mercury concentration.

3.3 The reporting limit for water matrix is 0.2ug/L and for soil is 0.1mg/kg. Current MDLs are listed in LIMS and are available from the Quality Department.

4. Interferences

4.1 Potassium permanganate ($KMnO_4$) is added to samples to eliminate possible interference from sulfide. Concentrations as high as 20mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10mg/L had no effect on recovery of mercury from spiked samples.

4.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25mL) because during the oxidation step, chlorides are converted to free chlorine, which also absorbs light at 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This maybe accomplished by using an excess of hydroxylamine hydrochloride reagent (25mL).

5. Safety

5.1 The toxicity and carcinogenicity of each reagent described in this document has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation

5.2 Analysts should take necessary safety precautions when handling chemicals and samples.

5.3 Proper personal protection equipment must include, at a minimum, a lab coat, gloves, and safety glasses.

5.4 Analysts should be familiar with the SDS sheets for all chemicals and reagents used in this procedure and the location of the SDS sheets within the laboratory.

5.5 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. The digestion must be conducted in a laboratory hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

5.6 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be performed in a fume hood.

5.7 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.8 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.9 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 Calibration Blank- A volume of reagent water acidified with the same acid matrix as found in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument. In this document, the calibration blank is equivalent to an instrument blank.

6.3 Batch- A set of no more than 20 samples, each of which is a well mixed aliquot of an aqueous solution. In addition to the samples, an MB, LCS, two Matrix spikes (MS) and two matrix duplicate (MD) samples are included.

6.4 Linear dynamic range (LDR)–The concentration range over which the instrument response to mercury is linear.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Because of the sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, extreme care must be taken to avoid extraneous contamination. Sampling devices, sample containers, and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

8.2 For the determination of total mercury (inorganic and organic) in aqueous samples, samples are not filtered, but are acidified with 1:1 nitric acid to pH<2 (normally, 3mL of 1:1 nitric acid per liter of sample is sufficient for most ambient and drinking water samples).

8.3 If dissolved mercury is to be determined, the sample is filtered through a 0.45µm filter using an all glass apparatus before the acid is added. Filtration and preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, it is recommended that the samples be returned to the laboratory as soon as possible after collection and are filtered and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed and then verified to be pH<2 just prior to withdrawing an aliquot for processing.

8.1.1 If for some reason, such as high alkalinity, the sample pH is verified to be >2, more acid must be added, and the sample held for 24 hours until verified to be pH<2.

8.4 The preserved sample must be prepared and analyzed within 28 days of collection.

8.5 A field blank should be prepared in the field and submitted for analysis as required by the data user. Use the same container and acid as used in sample collection.

8.6 Aqueous samples do not require thermal preservation.

8.7 Solid samples do require thermal preservation at ≤6°C.

9. Equipment and Supplies

9.1 Cetac Quick Trace Mercury Analyzer M-6100, or equivalent.

9.2 ASX-400 Autosampler, or equivalent.

9.3 Computer capable of running the QuickTrace® Mercury software, monitor, mouse, and keyboard.

9.4 Peristaltic pump and assorted peristaltic pump tubing.

9.5 Carrier Gas –Argon (99.999% purity).

9.6 Assorted glass and air-displacement pipettes.

9.7 Assorted volumetric flasks, class A, glass.

9.8 17 x 100 round bottom polystyrene culture tubes, or equivalent.

9.9 Version 1.7.6 QuickTrace® Mercury Analyzer Software.

10. Reagents and Standards

10.1 2% Hydrochloric Acid Solution (HCL): Pipette 20mL of Trace Metal grade concentrated Hydrochloric Acid into a 1000mL volumetric flask which contains approximately 500 – 600mL of DI water. Dilute to volume with DI water. This solution is used in the autosampler rinse station.

10.2 Stannous chloride: Weigh 35g stannous chloride, suitable for mercury analysis, into a 250mL beaker. In a fume hood, slowly add 50mL of Trace Metal grade concentrated hydrochloric acid. Using a hot plate, heat the solution until it is clear. Remove from the heat, cool and transfer into 500mL volumetric flask which contains approximately 250mL of DI water. Dilute to volume with DI water. This will yield a 7% stannous chloride in 10% HCl solution.

10.3 Hydroxylamine hydrochloride: Weigh 150g hydroxylamine hydrochloride into a 250mL beaker. In a fume hood, add approximately 100mL of DI water and gently heat on a hot plate heat until the solution it is clear. Remove from solution from the heat, cool and transfer into 1000mL volumetric flask which contains approximately 500mL of DI water. Dilute to volume with DI water. This will yield a 15% hydroxylamine hydrochloride solution.

10.4 DI (Millipore) Water (Type II)

10.5 A calibration curve is generated by analyzing the following standards: Calibration Blank(S1), 0.2µg/L(S2), 0.5µg/L(S3), 1.0µg/L(S4), 5.0µg/L(S5), 10.0µg/L(S6). Note: instructions for preparing these standards are found in the appropriate mercury preparation SOPs.

11. Calibration

11.1 A calibration curve is generated by analyzing the following standards: Calibration Blank(S1), 0.2µg/L(S2), 0.5µg/L(S3), 1.0µg/L(S4), 5.0µg/L(S5), 10.0µg/L(S6). Note: instructions for preparing these standards are found in the appropriate Hg preparation SOPs.

11.2 The response of the standards is plotted versus the concentration using linear regression. The correlation coefficient (r) must be ≥0.995.

11.3 The initial calibration verification (ICV) standard is purchased from a secondary source. The continuing calibration verification (CCV) standard is from the same source as the initial calibration curve, (typically the midpoint concentration).

12. Procedure

12.1 Turn on the computer and monitor.

12.2 Turn on the mercury analyzer and the autosampler. There are two black switches and two buttons that will need to be turned on. The two black switches lay on the bench top and the two buttons are located on the back right hand side of the mercury analyzer and autosampler. (One is for the mercury analyzer and one is for the autosampler).

12.2.1 Allow at least 15 minutes for the lamp to stabilize.

12.3 Add 2mL hydroxylamine hydrochloride to the aqueous mercury samples (and standards) and 3mL hydroxylamine hydrochloride to the solid and wipe mercury samples (and standards). Place the cap securely on each PDV and shake. This will clear the potassium permanganate and the samples will be ready for analysis.

12.3.1 After the solid and wipe mercury samples and standards have been cleared, allow them to sit for at least an hour so the solid portion of the sample can settle to the bottom of the PDV.

12.3.2 Before placing the PB, LCS, or any of the samples in the autosampler rack, fill the autosampler tube with the PB, LCS, or the sample and use a serum filter to remove any unsettled solids.

12.4 Place the bridge stops of the pump tubing in the channels on the posts of the peristaltic pump.

12.4.1 Place the drain tubing in the bottom two channels.

12.4.2 Place the tubing from the autosampler sipper in the third channel from the bottom.

12.4.3 Place the tubing from the reagent container in the top channel.

12.4.4 Clamp in the quick-release mechanisms.

12.5 Double click on the Quick Trace icon on the main computer screen.

12.5.1 The mercury analyzer will autozero itself.

12.6 Turn on the peristaltic pump. There is a switch on a black box on the bench top and a switch on the front left hand side of the peristaltic pump that will need to be turned on.

12.6.1 Make sure that the solutions are flowing and draining smoothly. Refer to the Quick Trace M-6100 Mercury Analyzer Operator Manual for proper flow.

12.7 Click on the Worksheet icon.

12.7.1 Click FILE.

12.7.2 Click OPEN.

12.7.3 Scroll over and double click on the masterworksheet that is associated with your name.

12.7.4 Minimize the QuickTrace software.

12.8 Double click on the Hg WLD Import icon.

12.8.1 Click IMPORT WLD.

12.8.2 Type the batch that will be run into the file name.

12.8.3 Example of a batch: MERC2125.

12.8.4 Click OPEN.

12.8.5 Highlight samples and use the up/down arrows to arrange the samples into the order that they will be run in.

12.8.6 Once the samples are in the correct order, click auto position and add cal/QC box.

12.8.7 Click SAVE LIST and name it with the batch number.

12.8.8 Example: MERC2125.

12.8.9 Close the Hg WLD Import.

12.8.10 Maximize the QuickTrace® software.

12.8.11 Right click on the blank sequence table and click IMPORT SAMPLE LABELS

12.8.12 Type in the batch that was saved in the Hg WLD Import.

12.8.12.1 Example: MERC2125.

12.8.13 Click OPEN.

12.8.14 Click FINISH

12.8.15 Click FILE

12.8.16 Click SAVE AS

12.8.16.1 Save the file in the QuickTrace software with Hg followed by the date.

12.8.16.2 Example: Hg021391.

12.8.17 Right click on the sequence table and click PRINT SAMPLE LABELS.

12.9 The center post of the gas-liquid separator (GLS) needs to be “wetted” before analysis can begin.

12.9.1 Unscrew the thumb-screw on the front of the mercury analyzer and open the front door.

12.9.2 Disconnect “11-HG Vapor-12” tube from the GLS vapor outlet.

12.9.3 Place the reagent sipper in a beaker of DI water.

12.9.4 Using the quick-release mechanisms, fully release the clamp tension on the bottom two channels (the drain channels) of the peristaltic pump.

12.9.5 Pinch the drain tube in front of the pump before the clamps.

12.9.6 With the drain pump tubes unclamped, the GLS should begin to fill with liquid. Once the liquid level rises, gas will bubble through it.

12.9.7 Allow the GLS to fill until a gas bubble propels a meniscus upward to wet the post all along its length, including its top.

12.9.8 When this happens, re-engage the quick-release clamps on the drain pump tubes and un-pinch the drain tube. With the drain tube clamps properly re-engaged and the pump running, the liquid will begin to drain.

12.9.9 Once the GLS has emptied, leave the pump running; reconnect “11-HG Vapor-12” tube to the GLS vapor outlet.

12.9.10 Close the front door on the mercury analyzer and tighten the thumb-screw.

12.9.11 Place the reagent sipper in the reagent container.

12.10 Pour the standards and samples into the correct locations in the standard and autosampler racks.

12.11 Click on the green GO icon to start the calibration and sample analysis according to the sequence screen that was just entered into the master worksheet.

12.12 Click OK to “Set gas flow to 30 PSI”.

12.13 When the analysis is complete and all the data are acceptable, the run can be printed and sent to the network.

12.13.1 Click on the REPORT icon.

12.13.1.1 Click on the worksheet file that needs to be printed to highlight it.

12.13.1.2 Click on the PRINTER icon to print the report.

12.13.1.3 The report will print at the copier.

12.13.2 Click on the DISK icon.

12.13.2.1 Click on the dropdown arrow and select the J drive.

12.13.2.2 Double click on METALS.

12.13.2.3 Double click on 30HG1.

12.13.2.4 Type in the file name to be saved.

12.13.2.5 Click on the dropdown arrow next to save as type and select text file.

12.13.2.6 Click SAVE.

12.13.3 Close the window.

12.13.4 Close the report screen.

12.14 Pull the sipper out of the reagent container and place it in DI water to clear all the stannous chloride out of the tubing.

12.15 Empty the standard and autosampler racks.

12.16 After 10-15 minutes, pull the sipper out of the DI water and raise the autosampler probe to allow them to dry completely.

12.17 Close all the windows and exit the QuickTrace® software.

12.18 Turn off the peristaltic pump, the autosampler, the mercury analyzer, and all the black boxes on the benchtop.

12.19 Turn off the computer.

12.20 Release the tension on the pump tubing with the quick-release mechanisms and release the bridge stoppers from the channels on the posts of the peristaltic pump.

13. Calculations

13.1 Percent Recovery/ (M% REC)/ % Recovery:

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} x100\%$$

NOTE: The SampleConc is zero (0) for theLCS Calculations

13.2 Relative Percent Difference (%RPD):

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} x100\%$$

Where:

R1 = Result Sample 1
R2 = Result Sample 2

13.3 Results Calculation:

13.3.1 Soil/solid samples- Assumes a final concentration of 25mL and an initial volume of 0.6g.

*Conc. (mg/Kg, wet) = Conc. In digestate (µg/L) * (F.V. sample /Initial mass)/1000*

Where:

F.V. = Final volume of the digestate (mL)

Initial mass = Initial mass of sample digested (g)

14. Quality Control

14.1 The Initial, Calibration Verification (ICV/QCS) must be analyzed following the instruments calibration. For the data to be considered valid, the ICV must be within ±10% of the stated value for methods 7470A, 7471A and 7471B. For method 245.1, the ICV must be within +5%. If the ICV is not within acceptable QC limits, reanalyze. If the reanalysis is out of control, terminate the analysis, fix any problems and recalibrate the instrument.

14.2 Calibration Blanks (ICB/CCB): Blanks are analyzed immediately following the ICV and CCV. The result must be lower than half the reporting limit. If the ICB/CCB is not within acceptable QC limits: reanalyze. If the reanalysis is out of control, terminate the analysis, fix any problems and recalibrate the instrument. The calibration standard S1 will be used for the ICB/CCB.

14.3 Continuing Calibration Verification (CCV): To be analyzed at a frequency of no more than 10 unknown samples. Data will not be accepted from an analytical run were samples are not bracketed by CCVs which have a % Recovery greater than ±10 % of the stated value. If the CCV is out of control, reanalyze. If the reanalysis is out of control, terminate the analysis, fix any problems and recalibrate the instrument. The calibration standard S5 will be used for the CCV.

14.4 Method Blank (PB): One (1) per batch of 20 unknown samples. The result must be lower than the reporting limit. If the PB is not within acceptable QC limits: reanalyze. If the reanalysis is out of control high, any samples that are less than the reporting limit or have a concentration 10 times the PB concentration may be reported with qualification in the final report. Otherwise re-preparation of the batch is required.

14.5 Laboratory Control Sample (LCS): One (1) per batch of 20 unknown samples. The result must be ±15% of the stated value for method 245.1 or +20% for methods 7470A and 7471B or within laboratory established limits. Any sample digested with an unacceptable LCS must be re-prepped and analyzed. LCS samples with results that are biased high and have sample concentrations less than the reporting limit may be reported with qualification in the final report.

14.6 Matrix Duplicate (MD): Two (2) per batch of 20 or at a frequency of 10% unknown samples. A % RPD of less than or equal to 20% is required, or the sample must be qualified in the final report.

14.7 Matrix Spike (MS): Two (2) per batch of 20 unknown samples or at a frequency of 10%. Recoveries of ±20% of the stated value or within laboratory established limits are required for method 7471B; +25% for method 7470A; and +30% for method 245.1. If the MS/MSD samples have unacceptable results and the associated LCS sample of the batch is analyzed with acceptable results, matrix interference may be assumed and the results of the batch may be reported with qualification in the final report.

14.8 CRDL Standard: A standard prepared during the digestion process, with the concentration at the reporting limit. It is analyzed after the ICB. For the data to be considered valid, the CRDL must be within ±50% of the stated value for methods 245.1, 7470A, 7471A and ±30% for method 7471B. If the CRDL is out of control, reanalyze. If the reanalysis is out of control, terminate the analysis, fix any problems, recalibrate the instrument and reanalyze the affected samples. The calibration standard S2 will be used for the CRDL. For some programs/client requirements, the CRDL is also analyzed at the end of the analysis.

14.9 Corrective Actions for Out-Of-Control Data

14.9.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.9.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.9.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and the results noted in the final report.

14.9.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.9.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.9.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.9.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.9.5.2 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit, and duplicate precision meets the acceptance criteria.

14.9.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 MDLs/LODs will be determined as stated in SOP PGH-C-035.

15.2 The requirements that must prior to the commencement of work, includes but is not limited to:

15.2.1 Reading and understanding the method and relevant SOPs,

15.2.2 Running an acceptable initial demonstration of capability (IDOC). For the IDOC, a analyst must be able to calibrate and run four (4) Laboratory Control Samples (LCS). The resulting average of these 4 LCSs must be within ±15% of the true value and also have a standard deviation of less than 10.

15.2.3 Running an acceptable blind performance evaluation sample.

15.3 Linear dynamic range (LDR) (for method 245.1 only): The upper limit of the LDR must be established. It must be determined from a linear calibration prepared from a minimum of 3 different concentration standards, one of which is close to the upper limit of the linear range. The LDR should be determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10% below the stated concentration of the standard. The determined LDR must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDR should be verified annually or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

15.4 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.5 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.6 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDS's.

16.2 All chemicals, reagents, and solutions should be used in a hood.

16.3 Where possible, dispense acids and solutions in bottles with a bottle top dispenser to avoid splashing and spills.

16.4 See the most recent revision of the Standard Operating Procedure for "Waste Management and Disposal".

17. References

17.1 Test Methods for Evaluating Aqueous Wastes (SW-846): Physical/Chemical Methods. Third Edition as Amended Through Update III, Method 7470A, Mercury in Liquid waste, Revision 1, September 1994.

17.2 Test Methods for Evaluating Solid Wastes (SW-846): Physical/Chemical Methods. Third Edition, Update III, Method 7471A, Mercury in Solid Waste, Revision 1, September 1994.

17.3 Test Methods for Evaluating Solid Wastes (SW-846): Physical/Chemical Methods. Third Edition, Update IV, Method 7471B, Mercury in Solid Waste, Revision 2, February 2007.

17.4 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 March 1979, Third Edition, Method 245.1, Determination of Mercury in Water.

17.5 Determination of Mercury in Water, EPA-600/R-94/111, May 1994, Supplement 1. Method 245.1 Revision 3.0, EMMC Version.

17.6 Cetac Mercury Analyzer Analysis Systems Manual.

17.7 SOP PGH-C-035, Determination of Limit of Detection and Limit of Quantitation.

17.8 SOP PGH-M-011, Aqueous Hg Digestion, current version.

17.9 SOP PGH-M-012, Solid Hg Digestion, current version.

17.10 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.11 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.12 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Not Applicable.

19. Maintenance

19.1 Change the pump tubing when necessary.

19.2 Clean the Optical Cell when necessary.

19.3 Replace the lamp when necessary.

19.4 Replace the GLS when necessary.

19.5 Replace the Nafion Dryer Cartridge when necessary.

19.6 Replace the 2-micron filter when necessary.

20. Method Deviations

20.1 None

21. Revisions

Document Number	Reason for Change	Date
PGH-M-017-4	Added references for SOPs PGH-M-011, Aqueous Hg Digestion and SOP PGH-M-012, Solid Hg Digestion.	3/6/14
PGH-M-017-5	1. Cover and Section 1.1: Updated method reference for 245.1. 2. Section 2.1: Specified extracts can only be run by 7470A. 3. Section 3.3: Added reference to current MDLs. 4. Section 14.1: Specified ICV limits per method. 5. Section 14.5: Specified LCS limits per method. 6. Section 14.7: Specified MS/MSD limits per method. 7. Section 15.3: Added LDR language from method 245.1. 8. General: made editorial corrections. 9. Document Reformatted.	02Jun2014

DESCRIPTION:

Mercury vapor in atmospheres.

SUMMARY:

This SOP describes the procedure to prepare samples for analysis of mercury vapor collected on passive dosimeters or active samples which collects onto a solid sorbent tube. Mercury is collected on solid sorbent (Hydrar® or Hopcalite) for both devices which has an irreversible affinity for mercury. A Nitric acid/Hydrochloric acid digestion allows the solubilization of elemental mercury. Samples are collected following NIOSH 6009 or OSHA ID-140. For analysis, refer to the most current version of SOP HGCVAA2.

SCOPE:

This SOP is applicable to the determination of mercury in air, wipe and bulk samples. Samples fall under the guidelines of OSHA ID-140 and NIOSH 6009.

DOCUMENT CONTINUITY:

This document replaces Braun Intertec Corporation SOP HGVAPOR, Rev. 1.

SIGNATURES:

Quality Manager Craig Foxhoven **Date** 3-2-15
Craig Foxhoven

Technical Lead _____ **Date** 3/2/15
Cynthia Schultz

General Manager _____ **Date** 3-2-15
Derrick Friedrich

1.0 PERSONNEL QUALIFICATIONS:

1.1 Personnel performing this procedure must be qualified per the requirements outlined in chapter 1 of the Pace Analytical Services, Inc. Industrial Hygiene Analytical Laboratory Quality Assurance Manual (QAM).

2.0 SAFETY:

2.1 Personnel performing this procedure must follow general laboratory safety practices as defined in chapter 1 of the QAM.

2.2 Follow standard laboratory safety procedures. Always wear a lab coat and safety glasses.

2.3 Review all Safety Data Sheets (SDSs) for chemicals used in this procedure.

2.4 Wear acid resistant gloves when handling acids.

2.5 A fume hood must be used during the digestion procedure.

2.6 Always add acid to water, not water to acid.

3.0 DEFINITIONS:

3.1 Refer to standardized Pace Analytical Services, Inc. definitions as described in Chapter 4 of the QAM.

3.2 HCl: concentrated hydrochloric acid.

3.3 HNO_3: concentrated nitric acid.

3.4 Hg: mercury.

3.5 STD: calibration standard.

3.6 Digestate: this refers to the sample extract once the sample itself has been processed through the digestion procedure.

3.7 LIMS: Laboratory Information Management System.

4.0 FORMS & RECORDS:

4.1 LIMS Bench Sheet; refer to Appendix A for an example (Bench sheets\BCH IH INORG 04.xx, 05.xx, or inorganics 14.xx).

4.2 LIMS Standard Record; refer to Appendix B for an example.

5.0 EQUIPMENT & SUPPLIES:

5.1 Various class A volumetric flasks.

5.2 50 mL plastic digestion vessel, or equivalent.

5.3 Calibrated auto-pipettor(s).

5.4 Whatman 41 filter paper or equivalent and disposable 50 mL beakers.

6.0 REAGENTS & STANDARDS:

6.1 Concentrated hydrochloric acid, trace metal grade or better.

6.2 Concentrated nitric acid, trace metal grade or better.

6.3 Calibration Stock Standard: Purchased 1000 µg/mL Hg standard provided by an approved vendor with the proper ISO 17025 and ISO Guide 34 Reference Material Producer credentialing.

6.4 Working Calibration Solution (1 µg/mL): Add approximately 50 mL to a 100 mL volumetric flask. Add 2 mL of concentrated HNO_3. Pipet 0.1 mL of purchased stock standard and dilute to the 100 mL mark. Record pertinent information in LIMS for traceability, expiration is 6 months from the preparation date or when a component of the reagent expires, whichever is sooner.

6.5 Second Source Stock Standard: Purchased 1000 µg/mL Hg standard provided by an approved vendor. This standard must be from a different manufacturer and/or lot number than the calibration stock.

6.6 Working Second Source Solution (1 µg/mL): Add approximately 50 mL to a 100 mL volumetric flask. Add 2 mL of concentrated HNO_3. Pipet 0.1 mL of purchased stock standard and dilute to the 100 mL mark. Record pertinent information in LIMS for traceability, expiration is 6 months from the preparation date or when a component of the reagent expires, whichever is sooner.

7.0 INTERFERENCES & PROCEDURAL LIMITATIONS:

7.1 Organic vapors such as acetone and benzene may cause positive interference by absorbing light at 253.7 nm. Chlorine and oxides of nitrogen also absorb light at 253.7 nm. If any of these interferences are suspected some sample must be run without reductants to check for background absorption.

8.0 SAMPLE ACCEPTANCE & HOLDING TIMES:

8.1 Samples need no preservation.

8.2 Sample holding time is 28 days at room temperature.

9.0 CALIBRATION & STANDARDIZATION:

9.1 Refer to the most current version of SOP HGCVAA2 for instrument calibration. The calibration standards and second source standards are prepped with the samples.

9.2 The instrument is calibrated using a blank and 5 points: 0.5, 1.0, 2.5, 5.0, and 10.0 µg/L. To prepare calibration standards, label the digest vessels with the LIMS information and pipet the following amounts of the working calibration standard.

Standard ID	Pipetted Amount (µL)	Final Volume (mL)
Cal 1 (0.5 µg/L)	25	50
Cal 2 (1.0 µg/L)	50	50
Cal 3 (2.5 µg/L)	125	50
Cal 4 (5.0 µg/L)	250	50
Cal 5 (10 µg/L)	500	50

9.3 From this point forward, the standards are handled like samples.

Note: It is not necessary to prepare calibration standards with each batch; coordinate with the analyst.

10.0 PROCEDURE:

10.1 Dosimeter: Transfer sorbent into a labeled 50 mL digest tube while being careful not to lose any of the sorbent. Discard the screen and empty capsule.

10.2 Active Sampler: If a **prefilter was not used** during sampling, place the glass wool and sorbent into a labeled 50 mL digest tube. If a **prefilter was used** and the glass wool appears to contain Hopcalite or Hydrar®, the glass wool can be analyzed along with the sorbent; otherwise discard the glass wool plug. Carefully transfer the glass wool and sorbent to a labeled 50 mL digest tube while being careful not to lose any sorbent.

10.3 To the BLK2, BS and BSD sample tubes add clean, unused matrix to each tube if applicable.

10.4 Prefilter: Prepare as per method OSHA ID-145.

10.5 Transfer 2.5 mL concentrated nitric acid to the flask followed by 2.5 mL concentrated hydrochloric acid. [Note: To minimize loss of mercury through a

change in oxidation state, nitric acid is always added before the hydrochloric acid.] **Perform task in fume hood.**

10.6 Add standard solution to calibration standards and QC samples at this time. To the ICV/CCV, BS and BSD pipet 125 µL of the Working Second Source Solution.

10.7 Let samples sit for a minimum of one hour and swirling occasionally.

10.8 Bring the samples to volume with UPDI water.

11.0 CALCULATIONS:

11.1 Not Applicable.

12.0 DATA REDUCTION & RECORDS:

12.1 Document any deviations or non-conformances in accordance with the current quality assurance policies.

12.2 Deliver a copy of the bench sheet with the samples to the Inorganic Laboratory.

12.3 Samples are batched in LIMS. Sample volumes as well as all pertinent information regarding sample preparation, including standard IDs, are recorded in the bench sheet. Final data is entered into LIMS. QC calculations are performed by the LIMS.

13.0 REPORTING:

13.1 Data is reported following analysis; refer to applicable analysis SOP (HGCVAA2) for details.

14.0 QUALITY CONTROL:

14.1 Digest and analyze one reagent method blank and one matrix method blank for each batch of up to 20 samples. If analysis of the blank shows contamination, any samples that have results above the reporting limit and less than ten times the level of contamination, shall be footnoted.

14.2 Digest and analyze at least one Laboratory Control sample (LCS) and Laboratory Control Sample Duplicate (LCSD) with each batch of samples.

15.0 METHOD PERFORMANCE:

15.1 Refer to the appropriate analysis SOP (HGCVAA2) for information on method performance.

15.2 Since there currently is no proficiency test for this analysis, analysts are required to perform internal Demonstrations of Competency (DOCs) as described in the current version of QADOC06.xx.

15.3 Refer to Appendix C for factors of measurement uncertainty.

16.0 DETECTION LIMITS:

16.1 Refer to the appropriate analysis SOP (HGCVAA2) for information on method performance.

17.0 REFERENCES:

17.1 PRIMARY REFERENCES:

17.1.1 Occupational Safety and Health Administration Method OSHA ID-140, June 1991.

17.2 SECONDARY REFERENCES:

17.2.1 National Institute of Occupational Safety and Health - NIOSH method 6009, Issue 2, August 15, 1994.

17.2.2 Occupational Safety and Health Administration Method OSHA ID-145, December 1989.

18.0 WASTE MANAGEMENT & POLLUTION PREVENTION:

18.1 Please refer to the general policies and procedures outlined in chapter 7 of the QAM regarding waste management and pollution prevention.

18.2 Be sure to dispose of acid waste in the acid neutralization sink.

19.0 REVISIONS:

19.1 Major changes to this document are summarized in the table below.

Document ID	Changes made	Effective Date
HGVAPOR, Rev. 2	Changed from Braun Intertec format to Pace Analytical Services, Inc. format	02/26/15
	Added section 19.0 on major revisions	02/26/15
	Added second source standard to section 6.0	02/26/15
	Added batch QC clarification to section 14.1	02/26/15

Appendix A
Example LIMS Bench Sheet

PREPARATION BENCH SHEET

B5B0085

Pace Analytical Services, Inc. (IH Laboratory)

Prepared using: IHMETALS - OSHA ID-140 **Printed: 2/26/2015 11:54:12AM**

Matrix: Monitor

Lab Number	Prepared	Initial (Monitor)	Final (mL)	Spike ID	Time (min)	uL Spike	Comments
1500349-01	02/24/15 09:14	1	50		298 min		
OSHA ID140 MERCURY Ab							
1500349-01RE1	02/24/15 09:14	1	50		298 min		Added 2/24/2015 by CJS
OSHA ID140 MERCURY Ab							Added 2/24/2015 by CJS
1500349-02	02/24/15 09:14	1	50		298 min		
OSHA ID140 MERCURY Ab							
1500349-02RE1	02/24/15 09:14	1	50		298 min		Added 2/24/2015 by CJS
OSHA ID140 MERCURY Ab							Added 2/24/2015 by CJS
B5B0085-BLK1	02/24/15 09:14	1	50		min		
B5B0085-BLK2	02/24/15 09:14	1	50		min		Matrix Blank
B5B0085-BS1	02/24/15 09:14	1	50	4L12002	min	250	
B5B0085-BSD1	02/24/15 09:14	1	50	4L12002	min	250	
B5B0085-SRM1	02/24/15 09:14	1	50	4L12002	min	25	NMatrix MRL

Reagent	Description
4F19004	Nitric Acid (Trace metal grade)
4G11021	Hydrochloric Acid (Trace Metals Grade)
4L12002	Hg ICV Stock, 1 ppm

Bench sheets\BCH 05.01

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Appendix B
Example LIMS Standard Record

Analytical Standard Record

Pace Analytical Services, Inc. (IH Laboratory)

4L12002

Description:	Hg ICV Stock, 1 ppm	Expires:	06/10/15
Standard Type:	Analyte Spike	Prepared:	12/12/14
Solvent:	2% HNO3	Prepared By:	Cynthia Schultz
Final Volume (mls):	100	Department:	IHMETALS
Vials:	1	Last Edit:	12/26/14 09:00 by CJS

Stored in Prep Lab

Analyte	CAS Number	Concentration	Units
Mercury Vapor	7439-97-6	1	ppm
Mercury Replicate C	7439-97-6	1	ppm
Mercury Replicate B	7439-97-6	1	ppm
Mercury Replicate A	7439-97-6	1	ppm
Mercury	7439-97-6	1	ppm

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
4H05014	Hg Second Source Stock	08/05/14	** Vendor **	12/01/15	12/26/14 08:19 by CJS	0.1

Reviewed By Date

Standards\STD 01.02

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Appendix C
Factors of Measurement Uncertainty

Contributors to Measurement Uncertainty

SOP Name HGVAPOR

Reference Method NIOSH 6009, OSHA ID-140

Matrix Filters/Air tubes

Measuring Instruments	Representative and Applicable QC Data	Comments to Clarify Contributor Effects
Transportation/Storage/Handling:		
shipping time, container and temperature	NA	Limited impact on air samples from transportation, storage or normal handling.
lab storage time, conditions and temperature	NA	Usually no impact if recommended storage conditions and holding times in reference methods are maintained.
contamination in lab storage areas	NA	Usually no impact if recommended storage conditions and holding times in reference methods are maintained.
Laboratory Subsampling:		
sample nonhomogeneity	NA	Not applicable to sorbent tube and vapor analysis.
blending techniques	NA	Not applicable to sorbent tube and vapor analysis.
sample size	NA	Not applicable to sorbent tube and vapor analysis.
Sample Preparation:		
volumetric glassware	BS/BSD, DUP	NA for Class A; applies for graduated tubes or cylinders, digestion tubes, etc.
dispensing device	BS/BSD, DUP	Pipettes, Reagent dispensers and Pipetters that are not Class A.
balance	BS/BSD	Balance error is often insignificant compared to other MU sources.
temperature	BS/BSD, DUP	Hot Block Temperature variation between spots
sample extraction	BS/BSD, DUP	Applies to BS/BSD as it goes through the entire sample preparation process.
extractant background	BS/BSD, DUP, MB	Analyte or interferant is present in acids, solvents, etc.
Lab Environmental Conditions:		
temperature variance	NA	Not applicable to sorbent tube and vapor analysis.
humidity variance	NA	Not applicable to sorbent tube and vapor analysis.
Analysts:		
different analysts	BS/BSD, DUP	BS/BSD results reflect variability due to different analysts, as applicable, on different days.
analyst training level and experience	BS/BSD, DUP	BS/BSD results reflect variability due to different analysts, as applicable, on different days.
data interpretation by analyst	BS/BSD, DUP	BS/BSD results reflect variability due to different analysts, as applicable, on different days.
Measuring Instruments:		
instrument stability	BS/BSD, DUP	BS/BSD results reflect instrument variability on different days.
carryover effects	BS/BSD, DUP	Impact of high samples on following sample readings; can be monitored by proper use of instrument blanks.
day to day calibration differences	BS/BSD, DUP	BS/BSD results reflect instrument variability on different days.
interferences	BS/BSD, DUP	Analyte or interferant in solvents or other prep reagents used, etc.
Calibration Standards/Reference Materials:		
preparation variances	BS/BSD	Due to analysts, balances, dispensing devices used, etc.
calibration stock material uncertainty	CERTIFICATE	Obtain from certificate or estimate.
LCS reference material uncertainty	BS/BSD	LCS data not adjusted.
Test Procedure Variations:		
variation within and between reagent lots	BS/BSD, DUP, MB	Analyte or interferant is present in acids, solvents, etc.
extraction or digestion times, temperatures, and conditions	BS/BSD, DUP, MB	Batch QC results reflect variability due to any variations.
sample dependent modifications	BS/BSD, DUP, MB	Batch QC results reflect changes in conditions due to sample size, customer requests, etc.
desorption efficiencies within and between lots for sorbents	BS/BSD, DUP, MB	Batch QC results reflect variability due to any variations.
Data Manipulation:		
sampling media/blank correction	BS/BSD, MB	BS/BSD subjected to same treatment as customer samples.
instrument blank correction	BS/BSD/DUP	Auto Zero on instrument blank.
accuracy of calculations	BS/BSD/DUP	BS/BSD and DUP subjected to same treatment as customer samples.
area or air volume sampled	NA	Laboratory uses information provided by clients.

Where:

DUP = Duplicate, resulting from replicate sampling (NOTE: NOT LCS/LCSD duplicate spiked sampling media)
FB = Field Blank
FS = Field Spike - Not typically conducted unless part of sampling method validation. Should be considered only when laboratory is responsible for field sampling.
BS/BSD = Laboratory Control sample, matrix matched and typically taken through the entire analytical process with each sample batch
MB = Method or Matrix Blank
NA = Not Applicable
CERTIFICATE = Certificate of Analysis

STANDARD OPERATING PROCEDURE

Cyanide; Free, Total, and Amenable

Methods: EPA 335.4, EPA 9010C, 9012B, 9013, 9014 and SM 4500-CN- A., B., C., E., G., and I

SOP NUMBER:	PGH-I-053-12
REVIEW:	Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-053-11
REVIEW DATE:	Upon Procedural Change

APPROVALS

Penelope J Westrick Assistant General Manager	1/28/15 Date
Maureen K. Rokitnicki Senior Quality Manager	3/10/15 Date
Brayan Hampton Department Manager/Supervisor	3/3/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

TABLE OF CONTENTS

1. Purpose

1.1. This SOP provides the procedure for the extraction and determination of Free (Weak Acid Dissociable), Total, and Amenable (to chlorination Cyanide), in water, soil, and reactive scrubber solution samples by EPA Methods 335.4, 9010 B/C, 9013, 9014 and SM 4500 CN A/B/C/E/G/I.

1.2. LIMITATIONS: All NPDES and non-potable water samples that are submitted to the laboratory for free cyanide analysis must be sent to an approved contract lab for analysis by an appropriate method (i.e., OIA-1677, ASTM D7237-10, ASTM D4283-02). If a client requests free cyanide by SM 4500 CN-I for non-potable water for non-NPDES work, the laboratory may analyze it and report it with an N2 flag as non-certified parameter.

1.3. However, if the client states the sample is for compliance work under 40 CFR 136, then one of the promulgated methods must be used.

2. Scope and Application

2.1. This procedure applies to surface, and ground water; domestic and industrial waste (including organic waste); leachates (TCLP, SPLP, and ASTM) and solid samples.

2.2. This procedure may be used for the determination of total, amenable, and free cyanide.

2.3. This procedure gives separate preparation steps for the determination of total, amenable, and free (weak acid dissociable) cyanide. The determinative step is used to determine the concentration of cyanide from all of the preparation steps included in this method. In addition, the determinative method is used to measure the concentration of cyanide in the distillates resulting from the reactive cyanide method. The SmartChem® instrument, a discrete analyzer, is used to determine cyanide by EPA method 9014 and SM 4500-CN. The Lachat, an automated continuous flow analyzer, is used for analysis of cyanide by EPA methods 335.4 and 9012B.

2.4. Method SM 4500-CN I is used for analysis of free cyanide for PA samples as per PA regulations.

2.5. The reporting limit for total cyanide in aqueous samples is 0.01mg/L.

2.6. The reporting limit for amenable cyanide in aqueous samples is 0.01mg/L

2.7. The reporting limit for free cyanide in aqueous samples is 0.01mg/L

2.8. The reporting limit for total cyanide in solid and organic waste samples is 1.0mg/Kg.

2.9. The reporting limit for amenable cyanide in solid and organic waste samples is 1.0mg/Kg.

2.10. The reporting limit for free cyanide in solid and organic waste samples is 1.0mg/Kg.

2.11. An MDL Study or LOD verification is determined annually , unless otherwise specified by method or program, and must meet the criteria set forth in 40CFR part 136 Appendix B and in Pace Analytical SOP for MDLs.

3. Summary of Method

3.1. The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of reflux-distillation under acidic conditions. The HCN is absorbed into a solution of NaOH. The cyanide is then converted to cyanogen chloride by reactions with chloramine-T, which subsequently reacts with pyridine barbituric acid to give a red-violet colored complex. The coloration is proportional to the CN concentration, and is quantified photometrically by discrete analysis against a standard curve.

3.2. Methods EPA 335.4 as well as 9012B should be analyzed on a flow injection instrument such as the Lachat. Methods SM 4500 as well as 9014 should be analyzed on the Smartchem®, automated spectrophotometer.

4. Interferences

4.1. Oxidizing agents, such as chlorine, decompose some cyanides. Test a drop of sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06g ascorbic acid for each liter of sample volume.

4.2. Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during distillation should be treated by the addition of bismuth nitrate. The addition of a small amount of bismuth nitrate to the sample, prior to distillation, will precipitate out any sulfides to remove potential interferences.

4.3. The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser.

4.3.1. If antifoam is added to any sample, it must also be added to the batch method blank (MB) and LCS samples.

4.4. Nitrates and nitrites may form HCN during total cyanide distillation. This is prevented by the addition of sulfamic acid to the sample before the addition of the concentrated sulfuric acid.

4.5. For amenable cyanides, some organic chemicals may oxidize during chlorination to form breakdown products resulting in higher results for cyanide after chlorination than before chlorination. This may lead to a negative value for amenable cyanide. This is particularly true in samples from the steel industry, petroleum refining, and pulp and paper processing.

5. Safety

5.1. Samples are usually preserved to a high pH with sodium hydroxide. Reagents also include concentrated H2SO4 (highly corrosive) as well as bismuth nitrate (highly toxic).

5.2. The distillation process must always be performed in a fume hood, as HCN is highly toxic.

5.3. Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.4. The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.5. Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1. MDL: Method Detection Limit.

6.2. LOD: Limit of Detection.

6.3. Total Cyanide: Total cyanide is defined as all of the cyanide compounds that can be converted to CN^- under strong acid/reflux conditions. This includes most simple cyanide compounds as well as many complex cyanide compounds.

6.4. Amenable cyanide: Amenable cyanide is defined as cyanide compounds that are amenable to chlorination.

6.5. Free cyanide: Free cyanide is defined as cyanide that is released upon exposure to a weak acid. (Also known as Weak acid dissociable cyanide).

7. Responsibilities and Distribution

7.1. General Manager/Assistant General Manager (GM/AGM)

7.1.1. The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2. The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2. Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1. The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2. The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3. The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3. Department Manager/Supervisor

7.3.1. The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2. The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3. The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4. The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4. Individual Staff

7.4.1. Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2. Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3. Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Sample collection: Samples are to be collected in 250mL plastic or glass containers.

8.2. Preservation: Aqueous samples must be preserved with sodium hydroxide to pH >12.

8.3. Storage: Samples must be stored at 4 $\pm$ 2°C and have a holding time of 14 days from the date of collection.

9. Equipment and Supplies

9.1. SmartChem® discrete analyzer.

9.2. SmartChem® Software version 3.0.66.

9.3. SmartChem® 60-cuvette set.

9.4. Microbloc distillation block, or equivalent.

9.5. Enviro Midi-Dist® distillation Cyanide glassware and tubing connections (See glassware setup diagram).

9.6. Volumetric flasks,50mL, 100mL, 500mL, 1L, and 2 L., Class A, glass.

9.7. Class A volumetric pipettes or air displacement pipette.

9.8. Disposable pipettes.

9.9. Graduated cylinders, Class A, glass.

9.10. Analytical balance.

9.11. Funnels, Buchner and filling.

9.12. P-4 filter paper.

9.13. 60mL plastic bottles for distillate.

9.14. Antifoam addictive, Dow Corning 544, or equivalent.

9.15. Aluminum foil.

9.16. Plastic specimen cups with lids.

9.17. pH test strips.

9.18. Hach Residual Chlorine DPD packets.

9.19. Lead acetate test strips.

9.20. Microbloc Tubes (Lachat)

9.21. Micro Dist Heating Block.

9.22. Microbloc tube press.

9.23. Lachat QuikChem® 8500, or equivalent.

9.24. Heat resistant gloves.

9.25. Timer.

9.26. Parafilm.

9.27. KI test strips.

9.28. Boiling chips.

9.29. Weighing dishes.

9.30. Glass fiber filter pads.

9.31. Bottles, various sizes.

9.32. Tumbler, extraction

9.33. Separatory funnel.

10. Reagents and Standards

10.1. Stock Solutions

10.1.1. Stock 1000mg/L Cyanide Solution: Dissolve .251g KCN and .2g KOH in 100mL of DI water. Standardize with 0.0192N $AgNO_3$. This solution is good for 6 months. This may also be purchased commercially. (e.g., Spex Certiprep Catalog # RSCN9-2Y, or equivalent) For commercially prepared stock, refer to manufacturer's expiration date.

10.1.2. Second source certified cyanide standard solution: (e.g., LabChem Catalog #LC13545-1, or equivalent) Refer to manufacturer's expiration date.

10.1.3. 10N NaOH, purchased commercially.

10.2. Standard Solutions

10.2.1. Standard Cyanide Solution (10mg/L): Using a Class A pipette, add0.5mL of the 1000mg/L CN stock (10.1.1) into a 50mL volumetric flask containing 1.25mL 10N NaOH, and dilute to volume with DI water. Mix well. This solution must be prepared daily.

10.2.2. Standard Cyanide Solution (1mg/L): Using a Class A pipette, add 10mL 10mg/L standard (see10.2.1) to a 100mL volumetric flask. Dilute to volume with 0.25N NaOH (see 10.3.1) and mix well. This solution must be prepared daily.

10.2.3. Second Source Standard Solution (10mg/L): Using a Class A pipette, add 0.5mL 1000mg/L CN^- second source stock (10.1.2) into 1.25mL 10N NaOH, dilute to volume with DI water and mix well. This solution must be prepared daily.

10.2.4. LCS/High Curve Point (HCP) solution (TV = 0.2mg/L): Using a Class A pipette, add 1.0mL of 10mg/L second source CN^- solution to a 50mL volumetric flask. Dilute to 50mL with DI water (adjusted to a pH >12 with a few drops of 10N NaOH) and distill as a sample. This solution must be prepared daily.

10.2.5. Low Curve Point (LCP) solution (TV= 0.08mg/L): Using a Class A pipette, add 0.40mL of 10mg/L primary source CN^- working solution to a 50mL volumetric flask. Dilute to 50mL with DI water and distill as a sample. This solution must be prepared daily.

10.2.6. Matrix Spike (TV= 0.1mg/L): Using a Class A pipette add 0.5mL of second source 10mg/L CN^- working solution to a 50mL volumetric flask containing 30mL of sample. Mix and dilute to mark with the sample and mix well.

10.2.7. CCV solution (TV=0.20mg/L): Using a Class A pipette, add 2mL of 10mg/L Primary source and dilute to 100mL with DI water. Mix well. . This solution is not distilled and must be prepared daily.

10.2.8. ICV solution (TV=0.10mg/L): Using a Class A pipette, add 10mL of 1.00mg/L of secondary standard solution and dilute to 100mL with DI water. Mix well this solution is not distilled. This solution must be prepared daily.

10.2.9. The CCV is prepared from the primary source in the same manner as calibration standards. ICV/LCS and MS are prepared from the secondary source.

10.3. Distillation and Preparation Reagents

10.3.1. 0.25N Sodium Hydroxide Solution: Dissolve 20g NaOH in DI water and dilute to 2L with DI water; or dilute 50mL of the10N NaOH solution to 2L with DI water. This solution is good for 6 months. This may also be purchased commercially.

10.3.2. 1.5N Sodium Hydroxide Solution for Micro distillation: Dissolve 60g NaOH in a 1L volumetric flask containing 700mL DI water. Stir to dissolve and dilute to the 1L mark.

10.3.3. cadmium carbonate. Purchased commercially.

10.3.4. Concentrated sulfuric acid. Purchased commercially.

10.3.5. Magnesium Chloride Solution: Weigh 1020g $MgCl_2 \cdot 6H_2O$ into a 1Lbeaker and add DI water to approximately the 1500 or 1600mL mark. When the crystals have dissolved, transfer the liquid and the washings to a 1Lvolumetric flask, and dilute to volume with DI water, mixing well. This solution is good for 6 months.

10.3.6. Sulfamic Acid Solution for midi distillation: Weigh 160g NH_2SO_3H into a 1Lvolumetric flask, dissolve and dilute to volume with DI water. Mix. This solution is good for 6 months.

10.3.7. Sulfamic Acid Solution for micro distillation: Weigh 9.6g of NH_2SO_3H into a 100mL volumetric flask, dissolve and dilute to volume with DI water. Mix the solution well. This solution is good for 6 months.

10.3.8. Acetate Buffer: Weigh 820g Sodium Acetate Trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in a 2.5L jar. Add 1000mL Glacial Acetic Acid and 1000mL DI water. Stir until dissolved. This solution is good for 6 months.

10.3.9. Zinc Acetate: Weigh 120g Zinc Acetate into a 2L volumetric flask. Dissolve and dilute to 2L with DI water. This solution is good for 6 months.

10.3.10. Methyl Red indicator, 0.02% Solution in Methanol: Refer to manufacturer's expiration date.

10.3.11. MicoDist® Releasing Agent (200mL of 7.11M sulfuric acid / 0.79M magnesium chloride): In the hood, place into a 1L volumetric flask 110mL DI water. Add 32.2g magnesium chloride hexahydrate (MgCl2·6H2O) and let it dissolve completely. Slowly add 75.7mL concentrated sulfuric acid, swirling and allowing to cool. HCl fumes will be released. Transfer the solution to the automatic pipette container. Place the assembled and calibrated pipette cap on loosely and allow the solution to cool to room temperature in the hood. When the solution is at room temperature, screw the cap on tightly. Prime the pipette and the solution is ready to use in the Cyanide-1 method. This solution is good for 6 months.

10.3.12. Calcium Hypochlorite. Weigh 5.0g Calcium Hypochlorite into a 100mL volumetric flask, dissolve and dilute to volume with DI water. Invert to mix. This solution is to be stored in an amber glass jar, in the dark, and is good for 1 month.

10.3.13. Sodium Arsenite. Weigh 2.0g sodium Arsenite into a 100mL volumetric flask, dissolve and dilute to volume with DI water. Invert to mix. This solution is good for 1 month.

10.3.14. Deionized (DI) water and n-hexane, suitable for oil and grease determination (EPA 1664 A).

10.4. SmartChem Discrete Analyzer Reagents

10.4.1. Sodium Dihydrogenphosphate, 1 M: Dissolve 138g sodium phosphate monobasic in 1L of DI water. Refrigerate this solution at 4ºC. This solution is good for 1 month.

10.4.2. Chloramine-T Solution: Dissolve 2.0g of water-soluble chloramine–T in 500mL of DI water. Prepare fresh daily.

10.4.3. Pyridine-Barbituric Acid Reagent: Add approximately 100mL of DI water to a 500mL volumetric flask and begin stirring. Weigh 7.5g barbituric acid and add to flask. Add 7.5mL of concentrated HCl, and then add 37.5mL pyridine. Stir until dissolved and dilute to 500mL with DI water. This reagent is stable for 6 months if stored in a cool dark place. However, it is advisable to prepare a new solution once a month to maintain a consistent concentration. Refrigerate this solution at 4ºC.

10.4.4. Acetic Acid: Make a 1:9 (Glacial Acetic acid:DI Water) solution for pH adjustment. Good for 1 year.

11. Calibration (SmartChem® discrete analyzer)

11.1. Prepare a curve by placing 4mL of 0.50mg/L STD into position 1 of the standard tray. Place 5 empty cups in the curve tray and the SmartChem® discrete analyzer will prepare the following curve points for you: 0.01, 0.05, 0.10, 0.20, and 0.30 mg/L,

11.1.1. Prepare a standard curve by plotting instrument response against concentration values. A calibration curve may be fitted to the calibration solution concentration/response data using regression techniques.

11.1.2. Calibration must have a correlation coefficient of 0.995 or better to pass.

11.2. The initial calibration and distillation procedure are verified by distilling and analyzing two standards prepared from the second source standard at concentrations near the high and low range of the curve, (e.g. 0.08mg/L, 0.20mg/L). If the distilled standard analyzed values do not agree within ±10 percent of the true values, the analyst should find and correct the cause of the apparent error before proceeding.

11.3. Verify continuing calibration with the analysis of a mid-range CCV (0.2mg/L) for each QC batch. The analyzed value must be within plus or minus 10% of the true value.

12. Procedure

12.1. Sample Pretreatment: Water

12.1.1. Add 1 packet of Residual Chlorine (DPD) chemicals to 10mL of sample. If the sample turns red/pink, this indicates the presence of chlorine and the sample must be treated. Record this result in the appropriate box of the distillation logbook. If a red/pink color is observed, add a few drops of sodium arsenite (SM 4500-CN E) to the sample and retest until no color appears.

12.1.2. Place a few drops of sample onto lead acetate paper. A black color indicates the presence of sulfide. Record this result in the appropriate box of the distillation logbook. See Section 4 for methods of removing this interference.

12.1.3. Place a few drops of the sample onto pH paper and record the initial pH. If the pH is <12, adjust the pH with a few drops of 10 N NaOH to a pH >12.

12.2. Distillation for Total Cyanide in Aqueous Samples using MIDI Block

12.2.1. Measure 50mL of sample or an aliquot diluted to 50mL with reagent grade water into the Enviro Midi-Dist® reaction flask. Add boiling chips and insert distillation head.

12.2.2. Add 50mL 0.25 N NaOH to the absorption flask (or 1.25mL 10 N NaOH and dilute to 50mL with DI water). If sulfide is present, add a small amount of cadmium carbonate to the absorption flask. Insert absorption impinger into absorption flask.

12.2.3. Refer to schematic for the appropriate placement positions and flexible tubing connections to assemble apparatus and cold finger into distillation block.

12.2.4. Repeat for all samples to be distilled up to 10 per distillation block.

12.2.5. Turn on condenser cooling water and vacuum source. Start a slow stream of air entering each reaction flask by adjusting each respective vacuum valve to provide an airflow bubble rate of several bubbles per second.

12.2.5.1. Note: the bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally to prevent the solution in the flask from backing up into the inlet tube, or the solution in the reaction flask from being drawn back into the absorption flask.

12.2.6. Add 2.5mL sulfamic acid solution through the inlet tube to remove possible interference from nitrates or nitrites.

12.2.7. Slowly add 2.5mL concentrated sulfuric acid through the inlet tube. -CAUTION: This addition can cause a violent reaction in some samples.

12.2.8. Rinse the inlet tube down with a very small amount of DI water.

12.2.9. Add 2mL of magnesium chloride solution into the inlet tube and wash it down the tube with DI water.

12.2.10. Turn the heat on and set the temperature of the heating block to 150 -160°C.

12.2.11. Set the timer and reflux for 90 minutes. Turn off the heat and continue the airflow for approximately 10-15 minutes while samples cool, until the heating block temperature is <100°C.

12.2.12. After cooling, disconnect the apparatus. Pour the contents of the absorption flasks into labeled 60mL plastic bottles for SmartChem® determination.

12.2.13. (Note: If cadmium carbonate was added to absorption flask, filter the sample solution through P4 filter paper into the bottle).

12.3. Distillation for Total Cyanide Samples using Micro Distillation

12.3.1. Set the controller to 120ºC. Allow the heater block to warm up. This will take about 40 minutes.

12.3.2. With the M end up; put the required number of cyanide-1 collector tubes into the collector tube rack.

12.3.2.1. For the user-filled collector tubes: fill the tubes with 1mL 1.5 N NaOH and cap the tubes.

12.3.2.2. For the pre-filled collector tubes: Use as is. Re-seal the foil pack after removing the tubes if it contains unused tubes.

12.3.3. Put the required number of sample tubes into the sample tube rack; up to 21 for one block. Place 6.0mL sample (or standard) into each sample tube with an automatic pipette.

12.3.4. For solid samples, weigh a 0.20-0.25g aliquot of soil or sludge with approximately 0.02g of cadmium carbonate. Add the sample to the tube along with 6mL of DI water.

12.3.4.1. The amount of cyanide in the soil or sludge in 6mL should be between about 0.012 and 600µg. If the sample is high in organics, a smaller sample size or less DI water may be required. Foaming or caking of the membrane is often eliminated by the above measures.

12.3.5. Add 0.25mL of the sulfamic acid solution to each sample tube to reduce nitrite interferences.

12.3.6. In order to both release the free cyanide as HCN and to digest complex cyanides during the digestion/distillation, first prime the re-pipettor several times into a waste container. Then, add 1.0mL of the 7.11M sulfuric acid / 0.79M magnesium chloride releasing solution to the sample tube using the supplied automatic pipette.

12.3.7. Immediately push the D end of Cyanide-1 collector tube over the open end of each sample tube to start the seal.

12.3.8. Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

12.3.9. The pressing motion should be a smooth constant pressure which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the D end of the collector tube.

12.3.10. Put on the heat-resistant gloves. Push the sample tube and D end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

12.3.11. Set the timer for 30 minutes.

12.3.12. When 30 minutes is up, put on the heat-resistant gloves. Remove the first tube from the block and immediately pull of the sample tube using a downward, twisting motion as opposed to a sideways motion. Remove the sample tube within 4 seconds of removing it from the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution left in it by dropping it into the sink or waste bucket.

12.3.13. Invert each collector tube and place it into the collector tube rack, with the D end up. The process of pulling and separating all 21 tubes should take less than 2 minutes.

12.3.14. Allow the tubes to cool for at least 10 minutes.

12.3.15. For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate. Then, slowly return the collector tube to an upright position so that the D end is up. Stubborn drops will often fall into M end when the tube is flicked with a finger.

12.3.16. With the D end still up, break the collector tube in half by pulling the D end hard towards the user to break it, then twisting and tearing off the D end. Discard the D end.

12.3.17. In the remaining M end of the collector tube, dilute the sample to the 6.0mL mark with DI water. This results in the original sample volume, but now in 0.25N NaOH.

12.3.18. Shake the tube with a gentle whipping motion to mix in diluent water. Do not invert the sample. With the M end down, place the tube into the collector tube rack.

12.3.19. Determine the concentration of the cyanide in the solution(s) on the SmartChem®. Seal both ends of the tube with Parafilm® if the sample will not be analyzed immediately.

12.4. Preparation and Distillation for Cyanides Amenable to Chlorination in Aqueous Samples

12.4.1. Measure out two 50mL aliquots of each sample and chlorinate one as in 12.3.2 below.

12.4.2. Place one aliquot into a 100mL beaker covered with aluminum foil (to eliminate light) and a foil wrapped watch glass to keep sample covered during chlorination. Add $Ca(OCl)_2$ solution drop wise to the sample while stirring. Test for chlorine with KI test strips. Sufficient chlorine is indicated by a distinct blue color. Maintain this excess of residual chlorine level for 1 hour while continuing to stir the sample. After 1 hour remove any residual chlorine from the sample by adding sodium arsenite solution dropwise. Test with KI strips until no blue is evident. (Alternately, specimen cups with lids, covered with aluminum foil may be used and shaken on a shaker table instead of using beakers and stir bars.)

12.4.3. Distill both the chlorinated and the un-chlorinated samples with the total-cyanide method (See Section 12.2)

12.5. Distillation for Free Cyanide (Weak Acid Dissociable) in Aqueous Samples

12.5.1. Measure 50mL of sample or an aliquot diluted to 50mL with reagent grade water into the Enviro Midi-Dist reaction flask. Add boiling chips and insert distillation head.

12.5.2. Add 50 0.25 N NaOH to the absorption flask. If sulfide is present, add a small amount of cadmium carbonate to the absorption flask. Insert the absorption impinger into absorption flasks.

12.5.3. Refer to schematic for the appropriate placement positions and flexible tubing connections to assemble apparatus and cold finger into distillation block.

12.5.4. Repeat for all samples to be distilled, up to 10 per distillation block.

12.5.5. Turn on the condenser cooling water and vacuum source. Start a slow stream of air entering each reaction flask by adjusting each respective vacuum valve to provide an air flow bubble rate of several bubbles per second. Note: the bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally to prevent the solution in the flask from backing up into the inlet tube, or the solution in the reaction flask from being drawn into the absorption flask.

12.5.6. Add 2.5mL acetate buffer solution through the inlet tube.

12.5.7. Add 2.5mL of zinc acetate solution through the inlet tube.

12.5.8. Add 3-4 drops of methyl red indicator solution into the inlet tube and wash down with stream of DI water.

12.5.8.1. If the sample does not turn pink, add (drop wise) the 1:9 acetic acid to the sample until a pink color persists.

12.5.9. Turn the heat on and set the temperature of the heating block to 150°C.

12.5.10. Set the timer and reflux for 90 minutes. Turn off heat and continue the airflow for approximately 10-15 minutes while samples cool.

12.5.11. After cooling, disconnect apparatus. Pour the contents of the absorption flasks into labeled 60mL plastic bottles for SmartChem® determination.

12.5.12. (Note: If cadmium carbonate was added to the absorption flask, filter the distillate through P4 filter paper into the bottle.)

12.6. Distillation for Free Cyanide (Weak Acid Dissociable) Samples using Micro Distillation.

12.6.1. Set the controller to 120ºC. Allow the heater block to warm up. This will take about 40 minutes.

12.6.2. With the M end up; put the required number of cyanide-1 collector tubes into the collector tube rack.

12.6.2.1. For the user filled collector tubes: fill the tubes with 1mL of 1.5N NaOH and cap the tubes.

12.6.2.2. For the pre-filled collector tubes: Use as is. Re-seal the foil pack after removing the tubes if there are any left.

12.6.3. Put the required number of sample tubes into the sample tube rack; up to 21 for one block. Place 6.0mL of sample (or standard) into each sample tube with an automatic pipette.

12.6.4. In order to release the free cyanide during the digestion/distillation, add 0.25mL of acetate buffer and 0.25mL of zinc acetate to each sample tube.

12.6.5. Add one drop of methyl red indicator solution to each sample tube. The samples should turn pink.

12.6.5.1. If a sample does not turn pink, add one drop of 1:9 acetic acid to the sample tube.

12.6.6. Immediately push the D end of Cyanide-1 collector tube over the open end of each sample tube to start the seal.

12.6.7. Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

12.6.8. The pressing motion should be a smooth constant pressure which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the D end of the collector tube.

12.6.9. Put on the heat-resistant gloves. Push the sample tube and D end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

12.6.10. Set the timer for 30 minutes.

12.6.11. When 30 minutes is up, put on the heat-resistant gloves. Remove the first tube from the block and immediately pull off the sample tube using a downward, twisting motion as opposed to a sideways motion. Remove the sample tube within 4 seconds of removing it from the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution left in it by dropping it into the sink or waste bucket.

12.6.12. Invert each collector tube and place it into the collector tube rack, with the D end up. The process of pulling and separating all 21 tubes should take less than 2 minutes.

12.6.13. Allow the tubes to cool for at least 10 minutes.

12.6.14. For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate. Then, slowly return the collector tube to an upright position so that the D end is up. Stubborn drops will often fall into M end when the tube is flicked with a finger.

12.6.15. With the D end still up, break the collector tube in half by pulling the D end hard towards the user to break it, then twisting and tearing off the D end. Discard the D end.

12.6.16. In the remaining M end of the collector tube, dilute the sample to the 6.0mL mark with DI water. This results in the original sample volume, but now in 0.25N NaOH.

12.6.17. Shake the tube with a gentle whipping motion to mix in diluent water. Do not invert the sample. With the M end down, place the tube into the collector tube rack.

12.6.18. Determine the concentration of the cyanide in the solution(s) on the SmartChem®. Seal both ends of the tube with Parafilm® if the sample will not be analyzed immediately.

12.6.19. For solid samples, weigh a 0.20-0.25g aliquot of soil or sludge with approximately .02g of cadmium carbonate. Add the sample to the tube along with 6mL of DI water. The amount of cyanide in the soil or sludge in 6mL should be between about 0.012 and 600µg. If the sample is high in organics, a smaller sample size or less DI water may be required. Foaming or caking of the membrane is often eliminated by the above measures.

12.7. Cyanide Extraction Procedure for Solids and Oils

12.7.1. If the waste does not contain any free liquid phase, go to step 12.7.5. If the sample is a homogenous fluid or slurry that does not separate or settle in the distillation flask when using a PTFE coated magnetic stirring bar but mixes so that the solids are entirely suspended, then the sample may be analyzed by Method 9012 without an extraction step.

12.7.2. Assemble the Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, and then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of DI water.

12.7.3. Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of DI water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

12.7.4. Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

12.7.5. Weigh the dish containing the solid, oil (if any), and filter pad. Subtract the mass of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

12.7.6. Place the following in a 1L wide-mouthed bottle: 500mL water, 5mL 50% w/v NaOH, 50mL n-Hexane (if a heavy grease is present). If the mass of the solids (step 12.7.5) is greater than 25g, weigh out a representative aliquot of 25g and add it to the bottle; otherwise, add all of the solids. Cap the bottle.

12.7.7. The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows: Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

12.7.8. Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

12.7.9. Prepare the Buchner funnel apparatus as in step 12.7.2 with a glass fiber pad filter.

12.7.10. Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

12.7.11. If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

12.7.12. At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be distilled and analyzed separately and concentrations given for each phase.

$$\frac{\text{Liquid Sample Aliquot(mL)}}{\text{Extract Aliquot(mL)}} = \frac{\text{Solid Extracted(g)}^{a}}{\text{Total Solid(g)}^{b}} \times \frac{\text{Total Sample Filtrate(mL)}^{c}}{\text{Total Extraction Fluid(mL)}^{d}}$$

a. From step 12.7.6. Mass of solid sample used for extraction.
b. From step 12.7.5. Mass of solids and oil phase with the dry mass of filter and tared dish subtracted.
c. Includes volume of all rinses added to the filtrate (steps 12.7.2 and 12.7.3)
d. 500mL water plus the total volume of NaOH solution. Does not include n-hexane, which is subsequently removed. (step 12.7.11)

Alternatively, the aliquots may be distilled and analyzed separately, concentrations for each phase reported separately, and the amount of each phase present in the sample reported separately.

12.8. Method 9012A Total and Amenable Cyanide (Automated Colorimetric, with Off-Line Distillation

12.8.1. Pretreatment for cyanides amenable to chlorination.

12.8.1.1. This test must be performed under amber light. $K_3[Fe-(CN)_6]$ may decompose under UV light, and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

12.8.1.2. To one 50mL sample or to a sample diluted to 50mL, add calcium hypochlorite solution drop wise while agitating and maintaining the pH between 11 and 12 with 1.25N NaOH until an excess of chlorine is present as indicated by a KI-test strip turning blue. The sample will be subjected to alkaline chlorination by this step.

12.8.1.3. Test for excess chlorine with a KI-test strip and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

12.8.1.4. After one hour, remove any residual chlorine by drop wise addition of 0.1N sodium arsenite until the KI-test strip shows no residual chlorine. Add 5mL of excess sodium arsenite to ensure the presence of excess reducing agent.

12.8.1.5. Test for total cyanide as described below in both the chlorinated and unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

12.8.1.6. If samples are known or suspected to contain sulfide, add 50mL of 0.06M cadmium carbonate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

12.8.2. Distillation Procedure

12.8.2.1. Place 50mL of sample, or sample diluted to 50mL in the back cyanide distillation tube. Pipette 50mL of 1.25N NaOH into the front scrubber. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

12.8.2.2. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

12.8.2.3. If samples are known or suspected to contain nitrate or nitrite, or if cadmium carbonate was added to the sample, add 5mL 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

12.8.2.4. Slowly add 5mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 2mL 2.5M magnesium chloride though the air inlet and wash the inlet tube with a stream of water.

12.8.2.5. Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

12.8.2.6. Transfer the solution from the scrubber into a 50mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with DI water.

12.9. Preparation and Distillation for Cyanides Amenable to Chlorination in Non-Aqueous Samples

12.9.1. Accurately weigh two representative 1g portions of sample. Add one aliquot to distillation flask and add 50mL DI water. Swirl sample to disperse. Adjust pH to >12 with a few drops of 10 N NaOH.

12.9.2. Add the other aliquot to a foil covered 100mL beaker and add 50mL DI water. Swirl sample to disperse. Adjust the sample to a pH >12 with a few drops of 10N NaOH. Use a foil wrapped watch glass to keep sample covered during chlorination. Add $Ca(OCl)_2$ solution drop wise to sample while stirring. Test for chlorine with KI test strips. Sufficient chlorine is indicated by a distinct blue color. Maintain this excess of residual chlorine for 1 hour while maintaining stirring of sample. After 1 hour remove any residual chlorine by drop wise sodium arsenite solution. Test with KI strips until no blue is evident.

12.9.3. Distill both the chlorinated and the un-chlorinated samples with the total cyanide method

12.10. Midi Distillation for Total Cyanide in Non Aqueous Samples.

12.10.1. Accurately weigh a representative 1g portion of sample and transfer into reaction flask. Dilute to 50mL with DI water. Swirl the sample to disperse.

12.10.2. Add a few drops of 10N NaOH to adjust pH to >12. Add a small amount of cadmium carbonate to each absorption flask.

12.10.3. Distill samples as described in a previous section on distillation of total cyanides in aqueous samples.

12.11. Midi Distillation for Free Cyanide (Weak Acid Dissociable) in Non Aqueous Samples.

12.11.1. Accurately weigh a representative 1g portion of sample and transfer into reaction flask. Dilute to 50mL with DI water. Swirl the sample to disperse.

12.11.2. Add a few drops of 10N NaOH to adjust pH to >12. Add a small amount of cadmium carbonate to each absorption flask.

12.11.3. Distill samples as described in a previous section on distillation of free cyanides in aqueous samples.

12.12. SmartChem® start up procedure

12.12.1. Go to SAMPLE ENTRY.

12.12.2. Double Click the METHOD RUN.

12.12.3. Enter the # of samples in the ACCEPT SAMPLES box.

12.12.4. Click on ACCEPT SAMPLES.

12.12.5. Enter Sample ID information.

12.12.6. Review the RUN PLANNER and click SAVE (red disk in upper right corner).

12.12.7. Go to SYSTEM MONITOR.

12.12.8. Click on the RUN PLANNER (the page in the upper left hand corner) that was created.

12.12.9. Verify that this is the correct run.

12.12.10. Load the samples, standards, controls, diluent, and empty cups as displayed in the System Monitor.

12.12.11. Check the probe rinse, DI water, and cleaning solution bottles.

12.12.12. Click START.

12.12.13. Click OK to run a water baseline (WBL). Cancel to skip the WBL.

12.12.13.1. A WBL should be obtained at least once each day.

12.13. Lachat 8500 procedure

12.13.1. Turn on the computer, autodiluter, pump, autosampler, and QuikChem® 8500 analyzer.

12.13.2. Double click on the OMNIONFIA 3.0 icon on the Windows® desktop. The QuikChem® 8500 will start and the autosampler will go through a quick test.

12.13.3. Once the program is open, Click on RUN, then OPEN, and select the Cyanide method.

12.13.4. The method will open on the screen displaying the tray list that corresponds with the order for the calibration standards, as well as the beginning QC set.

12.13.5. Right click the last sample number row that appears on the QC set (ICB) and insert the number of rows needed for samples and QC to complete the run.

12.13.6. Type in the sample identification in the appropriate order being sure that if a manual dilution was needed, to check the manual dilution box and enter the appropriate dilution factor. Ensure that after every ten samples a CCV, ICV, and Blank are analyzed to bracket the samples.

12.13.7. Verify that the proper manifold is on the analyzer and that all of the reagent lines are in the proper reagent bottle.

12.13.7.1. The correct manifold and reagent lines are specified in the Lachat Methods Manual.

12.13.8. Fill the autosampler tubes with sample that corresponds to the sample identification numbers input that appears on the screen. Sample tubes may be labeled with sample id's if needed.

12.13.9. Place the tray on the far left position of the autosampler with the number 1 tray position at the front left corner.

12.13.10. Check to ensure that empty tubes are in the tray on the right side of the autosampler for the autoanalyzed dilutions.

12.13.11. Be sure the peristaltic pump is set at a rate of 35 and click the levers into position by pushing down gently on each end of the lever until each end clicks, after both ends are in position gently pull the lever back to provide pressure on pump tubing.

12.13.12. Click to the RUN option on top left of the screen and select SAVE AS and name the run using the format month, day, year, the letter of the tray and then click OK.

12.13.12.1. For example, if 01 is the month 10 is the day 09 is the year and A is the first tray of the day then the file name would be entered as 011009A.

12.13.12.2. Click the START (Green Arrow) icon.

12.13.12.3. The calibration standards of the sequence will be analyzed first. The same calibration standards and criteria are used for both instruments. See Section 11.0.

12.13.12.4. If the calibration fails the system will stop the sequence and samples will not be analyzed.

12.13.12.5. The cause of the failure must be determined and resolved and the calibration must be reanalyzed.

12.13.13. When the initial calibration passes, the rest of the samples in the tray will be analyzed. Over range samples will automatically be diluted and reanalyzed. If samples are still over range manual dilution must be done.

12.13.14. When the analytical sequence is complete turn the pump off and if the day's runs are complete, flush the lines with DI water and drain them prior to shut down.

12.13.15. Note the height of the graph in millivolts, (y-axis) and the length of graph in seconds, (x-axis).

12.13.16. Click TOOLS, then CUSTOM REPORT, and select the options wanted for the hardcopy of the report.

12.13.17. Evaluate the results of the QC samples and the check standards against the acceptance criteria.

12.13.17.1. If the results are acceptable, submit the report for review.

12.13.17.2. Proceed to Section 14 (Quality Control) if the results of the QC samples or check standards are not acceptable.

12.13.18. System shut down procedure

12.13.18.1. Be sure to flush the lines as stated in Section 12.13.14.

12.13.18.2. Release the levers on the pump tubing by pushing in on the bottom of each side of the lever. The pressure will release and the lever will become free.

12.13.18.3. To shut the program down select RUN, then EXIT.

12.13.18.4. Shut off the auto diluter, pump, autosampler, and QuikChem® 8500 analyzer.

12.13.19. The software for the Lachat QuikChem® 8500 has an option to include peak areas along with the concentrations of each sample. This option is utilized with each and every batch of samples and is included with the printouts of the batch.

13. Calculations

13.1. Calculate the cyanide in the original sample as follows:

$$x\frac{y-b}{m}$$ Where:

y= Absorbance (optimum density)
m= Slope of the of the calibration curve
x= Concentration
b= Intercept

13.2. Duplicate Calculation (DUP): Relative Percent Difference (RPD)

$$RPD = \frac{|(R1-R2)|}{(R1+R2)/2} * 100$$

Where:

R1 = Result Sample 1
R2 = Result Sample 2

14. Quality Control

14.1. A batch is defined as 20 samples of the same matrix prepared and analyzed together on the same day.

14.2. A Method Blank (MB) must be analyzed with each batch and be < the Practical Reporting Limit (PRL). If contamination is found in the MB, the data are reviewed to determine the cause and the problem identified and corrected after which all associated batch samples must be reanalyzed.

14.2.1. The PRL for wastes and leachates is .01mg/L.

14.2.2. The PRL for solids and sludges is 1.0mg/Kg.

14.3. A – Laboratory Control Sample (LCS) must be included in each batch and have recovery within ± 10% of the true value. If limits are exceeded, associated batch samples must be reanalyzed.

14.4. A Duplicate analysis (DUP) must be performed once per batch Relative percent difference between the initial sample and duplicate must be within 20%. If exceeded, all batch samples must be reanalyzed unless the cause can be identified (i.e., extremely high or low cyanide concentrations in the sample).

14.5. A Matrix Spike (MS) must be analyzed once per batch with a recovery within ± 10% of the true value. A spike value outside of this range indicates the presence of possible matrix interference. If limits are exceeded, consult the LCS sample. If LCS sample is within limits, matrix interference is suspected and must be annotated. For method 9012B, MS and MSD must be distilled and analyzed with every 10 client samples.

14.6. Quality Control Table

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent (DI) water	One (1) per every 10 samples and one (1) at end of tray.	a) Target analytes must be less than reporting limit. PRL= 0.01mg/L.	1) Re-analyze associated samples. ***Exceptions:*** 1) If sample result is ND, report the result without qualification 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample result with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample data with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)/ High Curve Point (HCP)	Cyanide at a concentration of 0.2mg/L.	One (1) per batch of up to 20 samples.	% Rec within 90-110%.	1) Analyze a new LCS. 2) If the problem persists, check the spike solution 3) Perform system maintenance prior to a new LCS determination. ***Exceptions:*** 1) If LCS %Rec > QC limits, and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS) (2nd Source)	Cyanide at a concentration of 0.1mg/L	One (1) per batch of up to 20 samples.	% Rec within 90-110%.	1) If LCS and MBs are acceptable, the spike results should be reviewed and may be reported with appropriate footnote indicating matrix interferences
Continuing Calibration Verification (CCV) (Primary source)	Cyanide at a concentration of 0.2mg/L	One (1) at beginning, every 10 samples and one (1) at end of tray.	% Rec within 90-110%.	1) If CCV fails, reanalyze associated samples.
ICV (2nd Source)	Cyanide at a concentration of 0.1mg/L	One (1) at beginning, every 10 samples and one (1) at end of tray.	% Rec within 90-110%.	1) If ICV fails, reanalyze associated samples. ***Exceptions:*** 1) If ICV %Rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Duplicate Sample (DUP)	Cyanide	One (1) per every 20 samples.	RPD ≤ 20%	1) Reanalyze associated samples *Exceptions:* 1) If sample result is ND, report result without qualification. 2) If sample result is just above PRL and DUP is just below PRL, report without qualifications. If the difference between sample and DUP is 2x the detection limit, then samples do not need to be reanalyzed.

15. Method Performance

15.1. Reading and understanding the method and relevant SOPs.

15.2. Completion of an acceptable initial demonstration of capability (IDOC). Four aliquots of a Quality Control standard are analyzed.

15.3. Completion of acceptable semi-annual blind Performance Evaluation samples

15.4. Analysis of Method Detection Limits.

15.5. Analysis of in-house laboratory Quality Control samples.

15.6. LOD/LOQ

15.6.1. Total Cyanide (Aqueous)

LOQ	0.01mg/L		
LOD (or MDL)	0.00651mg/L	Effective 1/5/15	LOD subject to change

15.6.2. Total Cyanide (Solid)

LOQ	1.0mg/Kg		
LOD (or MDL)	0.184mg/Kg	Effective 11/7/14	LOD subject to change

15.6.3. Free Cyanide (Aqueous)

LOQ	0.01mg/L		
LOD (or MDL)	0.00301mg/L	Effective 3/4/14	LOD subject to change

15.6.4. Free Cyanide (Solid)

LOQ	1.0mg/Kg		
LOD (or MDL)	0.137mg/Kg	Effective 11/7/13	LOD subject to change

16. Pollution Prevention

16.1. Samples that have a high level of cyanide must be disposed of in appropriate containers.

16.2. Cadmium waste must be disposed of in appropriate waste containers.

17. References

17.1. “Methods for the Determination of Inorganic Substances in Environmental Samples”, USEPA Office of Research and Development, Cincinnati, Ohio, (EPA/600/R-93/100) EPA Method 335.4, Revision 1, August 1993.

17.2. SmartChem Method #281N-0405C (version).

17.3. Method 9010C, Total and Amenable Cyanide: Distillation, USEPA SW-846, Revision 3, November 2004.

17.4. Method 9013, Cyanide Extraction Procedure for Solids and Oils, USEPA SW-846, Revision 0, July, 1992.

17.5. Method 9014, Total and Amenable Cyanide: Distillation, USEPA SW-846, Revision 0, December, 1996

17.6. Method 9012B, Total and Amendable Cyanide (Automated Colorimetric, with Off-line Distillation. USEPA SW-846, Revision 2, November 2004.

17.7. Method 4500-CN- A (Introduction), B (Preliminary Treatment of Samples), C (Total Cyanide after Distillation), E (Colorimetric Method), G (Cyanide Amenable to Chlorination), and I (Weak Acid Dissociable Cyanide). Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

17.8. Method 4500-CN- A (Introduction), B (Preliminary Treatment of Samples), C (Total Cyanide after Distillation), E (Colorimetric Method), G (Cyanide Amenable to Chlorination), and I (Weak Acid Dissociable Cyanide). Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

17.9. Enviro Midi-Dist® Cyanide method.

17.10. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.11. TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.12. Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Figures, Attachments, Appendices

18.1. Attachment No. 1: Glassware set-up diagram.

18.2. Attachment No. 2: Micro Distillation Setup.

18.3. Attachment No. 3: Distillation Log.

18.4. Attachment No. 4: SmartChem® Flags.

18.5. Attachment No. 5: SmartChem® Cyanide Method Set-up Information.

19. Revisions

Document Number	Reason for Change	Date
PGH-I-053-10	1. Reporting limits changed to 0.01mg/L for aqueous samples for cyanide. 2. Calibration range changed by removing the 0.005 standard and adding 0.01 and 0.5mg/L standards. 3. Updated Attachment 6, SmartChem® parameters. SmartChem flags added.	04Mar2014

Document Number	Reason for Change	Date
PGH-I-053-11	1. Changed ppm to mg/L throughout document. 2. Purpose: Limitations to the method were included for non-potable water. 3. Edited for spelling and grammar. 4. Added to equipment list and reagent list per procedure. 5. Formatted document. 6. Added to section 1.1: LIMITATIONS: All NPDES and non-potable water samples that are submitted to the laboratory for free cyanide analysis must be sent to an approved contract lab for analysis by an appropriate method (i.e., OIA-1677, ASTM D7237-10, ASTM D4283-02). If a client requests free cyanide by SM 4500 CN-I for non-potable water for non-NPDES work, the laboratory may analyze it and report it with an N2 flag as non-certified parameter. However, if the client states the sample is for compliance work under 40 CFR 136, then one of the promulgated methods must be used.	27Jun2014
PGH-I-053-12	1. Updated cover page, headers and footers for this revision 2. Added “in the dark” to the storage conditions of the calcium hypochlorite reagent (10.3.12) to match method requirement. 3. Updated the MDL’s for the Total Cyanide in 15.6.1 and 15.6.2. 4. Added to the method deviation section: for method 9014 we use automated spec not manual.	22Jan2015

20. Equipment maintenance

20.1. SmartChem® Discrete Analyzer

20.1.1. Replace the sample needle as needed.

20.1.2. Replace the peristaltic pump as needed.

20.1.3. Replace the peristaltic pump tubing every 3 months.

20.1.4. Replace the cuvette drying pad as needed.

20.1.5. Replace the fluidics tubing as needed.

20.2. Lachat 8500 Flow Injection Analyzer

20.2.1. All maintenance must be recorded in the maintenance log book.

20.2.2. Replace the pump tubing when there are apparent leaks and/or the pump tubing is flattened, at least every three months.

20.2.3. Replace the manifold tubing when there are apparent leaks, clogs, or crimps within the tubing.

20.2.4. Replace the Lachat lamp when peaks are being suppressed and/or it is burnt out.

20.2.5. Replace the heater when the temperature is not reaching the correct programmed temperature and/or the heater malfunctions.

20.2.6. Replace the valve when it begins to stick and/or when air spikes are present instead of peaks.

20.2.7. Autosampler peak tubing is replaced when the autosampler begins to stick and/or the autosampler is not sampling correctly.

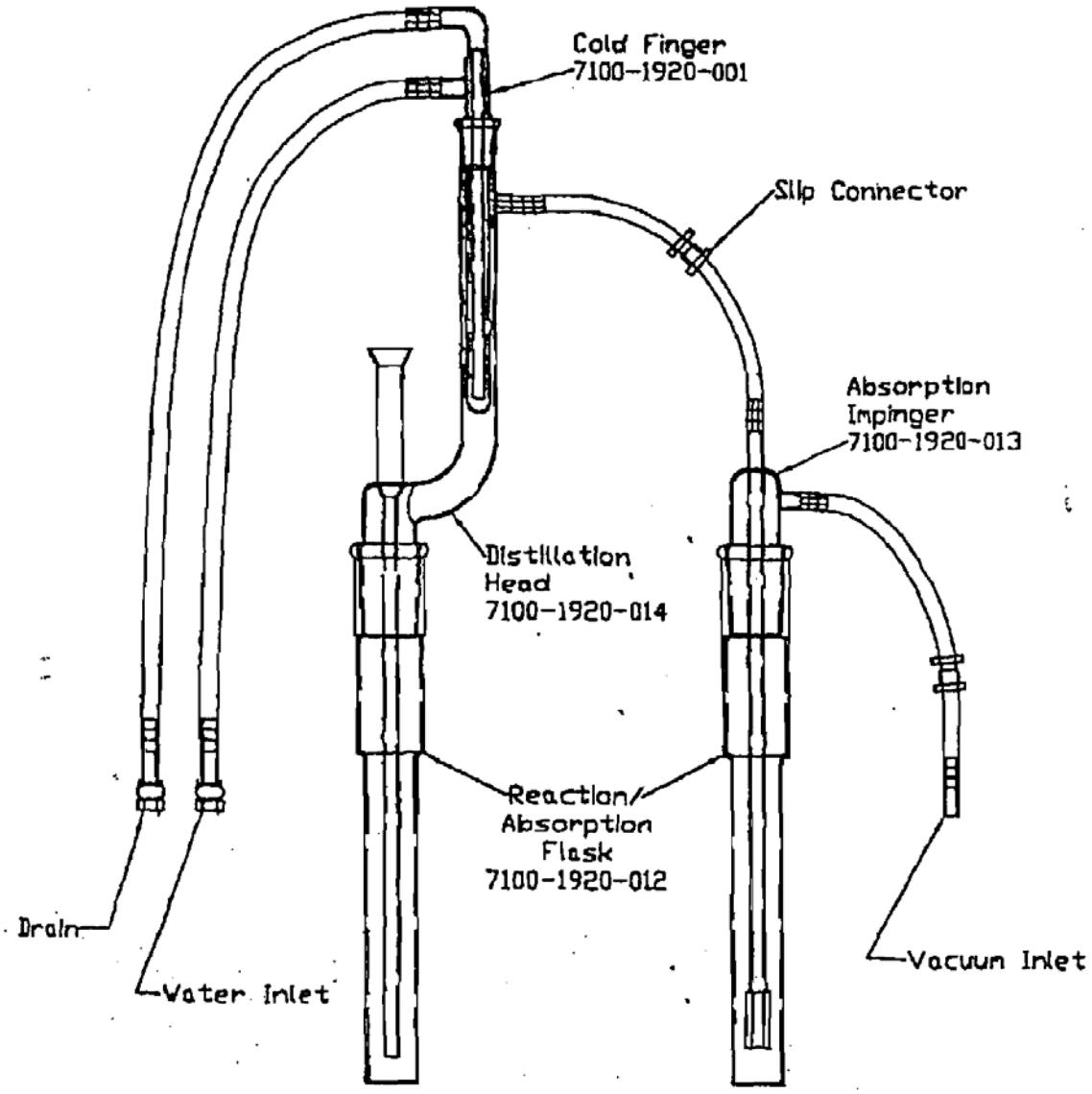
21. Method Deviations

21.1. Samples and reagents for the pretreatment of cyanides amenable to chlorination in method 9012A are used at 1/10 of their original volumes.

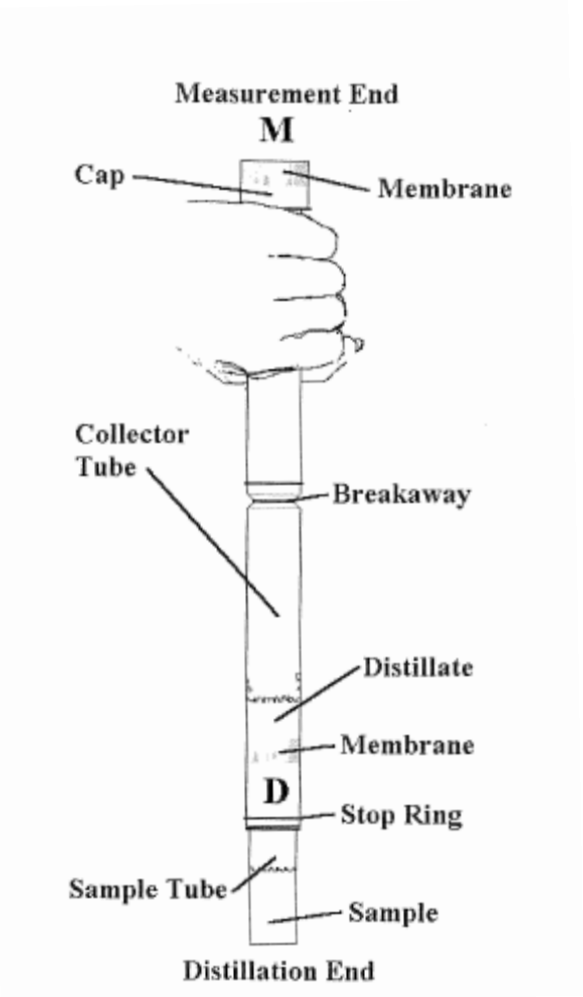
21.2. Method 9012A also describes a macro distillation method, whereas the actual methods used are for midi and micro based distillations as per sections 12.3 (Distillation for Total Cyanide Samples using Micro Distillation) and 12.10 (Midi Distillation for Total Cyanide in Non-Aqueous Samples).

21.3. Method 9014 refers to manual spectrophotometer. The lab uses automated spectrophotometer. All MDLs and DOCs are performed using the automated spec.

Attachment No. 1 - Glassware set-up diagram



Attachment No. 2 - Micro-Distillation Set up (Example)



Attachment No. 3 - Distillation Log (Example)

Pace Analytical

CN Distillation Log-Methods 335.4, 9010B/9014,9012, 4500CN-A,B,C,E,G,&I

	STANDARDS	REAGENTS
SOP.#PGH-I-007-1	Stock ID(1000 ppm)	Acetate buffer ID#
Batch#:	Working std ID(10ppm)	Zinc Acetate ID
Run#	mls wkg std added to:	Methyl Red ID#
Analyst:	LCS: TV=	Sulfamic Acid ID#
Prep Date:	MS: TV=	Sulfuric Acid ID#
Start Time:	MSD: TV=	MgCl2 ID#
Microbloc#1 ID#		NaOH ID#
Microbloc#2 ID#		Ascorbic Acid#
		Cadmium Carbonate ID#

Position	Project#	Sample#	Cyanide Type	Sample Matrix	Sample Wt.(g) or Vol.(ml)	Final Volume	pH	Sulfide present (Y or N)	Chlorine present (Y or N)
1-1									
1-2									
1-3									
1-4									
1-5									
1-6									
1-7									
1-8									
1-9									
1-10									
2-1									
2-2									
2-3									
2-4									
2-5									
2-6									
2-7									
2-8									
2-9									
2-10									

12-04 W:\shared\wetchem logs\cyanides.xls

Attachment No. 4 - SmartChem® Flags

SmartChem Flag Descriptions

TMP	Temperature Out of Range
SS	Short Sample
SR	Short Reagent
INV	Inversion
EPL	End Point Limit
D	Depletion Limit
FL	First Limit
NL	FIT
R	RBL Out of Range
><	OD Out of Calibration Curve
CV	CV% For Standard Replicates Exceeds Limits
CAL	Calibration Curve Exceeds Limit
L	LOW
H	HIGH
VL	Very LOW
VH	Very HIGH
LA	LOW Alert
HA	HIGH Alert
LL	Linearity LOW
LH	Linearity HIGH
CE	Calculation Error
E	EDIT

Attachment No. 5 - SmartChem® Cyanide Method Set-Up Information

CYN - CN 335.4/ SM 4500 E,G,I

Type	: End Point
Direction	: Up
Unit	: ppm
Model	: Linear
Unit Factor	: 1
Factor	: 1
Decimal	: 4
Slope	: 1
Intercept	: 0
Linearity Low	: 0
Linearity High	: 0.3
Filter 1	: 570
Fluidics	: Yes
Sample Blank	: No

RBL 1	: 0.0055
Rbl Replicate	: 3
Use RBL	: Yes
Rgt Rate 1	: 0.0000
E.P. OD Limit	: 0.0015

	Code	Vol	Delay	Read	Rinse
Reagent 1	BUFF	63	36	0	0
Reagent 2	CL-T	15	108	0	0
Reagent 3	PYR	150	0	504	0

	Concentration	OD		Concentration	OD
C1	0.01	0	C5	0.3	0
C2	0.05	0	C6	0.5	0
C3	0.1	0	C7	-	-
C4	0.2	0	C8	-	-

Diluent	: NAOH
Sample Vol	: 150
Dil/Ratio 1	: 1/10
Dil/Ratio 2	: 1/25
Dil/Ratio 3	: 1/50

Code	: CN
Description	: Cyanide
Lot#	: 010104
Exp Date	: 12/12/2050
User	: Westco Scientific
Cal Replicate	: 1
Std - Stock	: 0.5

STANDARD OPERATING PROCEDURE

Alkaline Digestion of Solid Samples for Hexavalent Chromium
Methods: EPA SW-846 3060A

SOP NUMBER:	PGH-I-066-1
REVIEW:	Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-066-0
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager — 07/06/15 Date

Senior Quality Manager — 07/06/15 Date

Department Manager/Supervisor — 07/06/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for performing an alkaline digestion on a solid sample for the determination of hexavalent chromium while meeting the requirements specified in EPA method 3060A.

2. Scope and Application

2.1 The digestion is applicable to soils, sediments, sludges and waste materials.

2.2 To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied:

2.2.1 The extracting solution must solubilize all forms of Cr(VI).

2.2.2 The extracting conditions must not induce the reduction of Cr(VI) to Cr(III).

2.2.3 The method must not cause the oxidation of Cr(III) in the sample to Cr(VI).

2.3 The alkaline conditions of the extraction minimize any oxidation and reduction. The accuracy of the extraction procedure is assessed using spike recovery data for soluble and insoluble forms of Cr(VI).

2.4 Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

2.5 This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of alkaline digestion equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Method

3.1 The alkaline digestion solubilizes both water-insoluble and water-soluble Cr(VI) compounds in solid samples. The pH of the digestate is critical and must be carefully adjusted throughout the digestion procedure. Failure to meet the pH specifications of this method will require redigesting of the sample.

3.2 The sample is digested using a sodium carbonate/ sodium hydroxide solution and heating at 90-95 °C for 1hour to dissolve the Cr(VI) and minimize the reduction to Cr(III). Cr(VI) content is determined using Method 7196A.

4. Interferences

4.1 When analyzing a sample digestate for Cr(VI), it may be necessary to determine the reduction/oxidation tendency of the sample. This can be done using several different methods including pH (Method 9045), sulfides (Method 9030), Oxidation/Reduction potential (ASTM method D1498-93), Total Organic Carbon (TOC), Chemical Oxygen Demand (COD); EPA method 410.4). These additional parameters can establish the tendency of Cr(VI) to exist or not exist in a sample.

4.2 Refer to method 7196A for any interference that may cause difficulties with the performance of the determinative steps following the digestion procedure.

4.3 For solids containing soluble Cr(III) in concentrations greater than 4 times the reporting limit for Cr(VI), Cr(VI) results may be biased high. The addition of magnesium in a phosphate buffer has been shown to suppress this oxidation in this digestion procedure.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

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7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

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7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

Table 8.1- Sample Collection, Preservation, Storage and Holding time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Solid	>100g in a glass container	None required	0°C to 6°C	Samples must be digested within 30 days of collection date and digestates must be analyzed within 7 days of digestion date.

9. Equipment and Supplies

9.1 Spectrophotometer set at 540 nanometers (Hach DR-5000 or equivalent).

9.2 1 centimeter (cm) absorption cell.

9.3 150mL beakers.

9.4 Funnels.

9.5 Filter paper (Fisher P4 or equivalent).

9.6 Class A volumetric flasks, 50mL, 100mL, 200mL, 1L Class A, glass.

9.7 Hot plate with stirrer.

9.8 Volumetric pipettes (assorted volume as necessary), Class A.

9.9 Magnetic stir bars.

9.10 Watch glasses.

9.11 pH meter (Thermo Orion 710, or equivalent).

9.12 Class A Graduated cylinder, 100mL.

9.13 Analytical balance, accurate to 0.01g.

9.14 IPAQ (see IPAQ SOP for instructions).

9.15 ORP Equipment:

Equipment	Model / Version	Description / Comments
pH meter	Thermo Orion 710 or equivalent	Must be capable of reading to 0.5 pH units
Platinum Pin Ag/AgCl Combination Electrode	Accumet 13-620-81 or equivalent	Platinum indicator, Ag/AgCl reference element, or equivalent,
Temperature probe	Fisher or equivalent	
Balance	Ohaus or equivalent	Accurate to 0.1g
ORP Meter	Ecosense ORP 15A	ORP range -1100 to 1100 mV

10. Reagents and Standards

10.1 Acetone (Fisher Optima® grade or equivalent).

10.2 Digestion Solution – Dissolve 20.0g sodium hydroxide (NaOH,ACS grade) and 30.0g sodium carbonate (Na_2CO_3, ACS grade) in 700mL deionized water and dilute to

1000mL in a 1000mL volumetric flask. The pH of this solution must be 11.5 or greater. This solution has a 1 month expiration.

10.3 Primary Stock Chromium (Cr^{+6}) Solution (500mg/L): In a 100mL volumetric flask, dissolve 141.4mg potassium dichromate ($K_2Cr_2O_7$,ACS grade) in DI water and dilute to volume with DI water. This solution is good for a maximum of 6 months.

10.4 Secondary Stock Chromium (Cr^{+6}) Solution (500mg/L): In a 100mL volumetric flask, dissolve 141.4mg potassium dichromate ($K_2Cr_2O_7$) {from a source other than that used for the primary stock solution}(ACS grade) in DI water and dilute to volume with DI water. This solution is good for a maximum of 6 months.

10.5 Standard Cr+6 Solution(s): In a 250mL volumetric flask, dilute 2.5mL of the stock Cr+6 solution to volume with DI water (5mg/L) This solution is good for a maximum of 1month. Prepare both a primary and secondary solution from the stocks listed above.

10.6 Diphenylcarbazide Solution: Dissolve 1.25g 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide, ACS grade) in acetone and dilute to 250mL with acetone in a 250mL volumetric flask. Store in an amber bottle. Expires one week after preparation or if solution becomes discolored.

10.7 1:1 Sulfuric Acid: Dilute 100mL con H2SO4 (Fisher purchased solution or equivalent) with a 100mL graduated cylinder to 200mL with DI water in a 200mL volumetric flask.

10.8 Magnesium Chloride (MgCl2) anhydrous: ACS grade.

10.9 Phosphate Buffer (0.5M K2HPO4/0.5M KH2PO4 buffer at pH 7): Dissolve 87.09g K2HPO4 and 68.04g KH2PO4 into 700mL DI water and dilute to volume in a 1L volumetric flask.

10.10 Concentrated Nitric acid: Trace metal grade, or equivalent. If the Nitric Acid has a yellow color this is indicative of photoreduction of nitrate ions to nitrite, a reducing agent for Chromium VI. Do not use this acid.

10.11 Lead Chromate for insoluble matrix spike: Reagent grade crystalline; store at room temperature, under dry conditions, in a tightly sealed container. The insoluble matrix spike is prepared by adding 12mg of PbCrO4 to a separate sample aliquot.

10.12 Sulfuric acid - Concentrated, reagent grade, JT Baker/ catalog # 9673-33 or equivalent

10.13 YSI 3682 Zobel Solution - Dissolve entire bottle of purchased solution in DI water in a 125ml volumetric flask. Used to calibrate the ORP meter.

11. Calibration

11.1 A standard curve is prepared by entering the absorbance values of the standards and the corresponding Cr+6 concentrations into the HEX-CHROME spreadsheet, refer to SOP PGH-I-012, Hexavalent Chromium Analysis. This spreadsheet performs a linear regression on the data and displays the regression statistics. The correlation coefficient (r) must be greater than or equal to 0.995.

11.2 The solid calibration curve is prepared using the same curve points, except for the 0.01mg/L standard. The curve is digested following the same procedure as the samples using 2.5g of glass beads.

11.3 Prepare the standards and a blank by pipetting suitable volumes of the 5mg/L Working Standard Solution into a 150 mL volumetric flask containing 2.5 g of beads.

Volume of 5mg/L Working Standard (ml)	Concentration (mg/kg)
0.5	1
1	2
2	4
5	10
10	20
15	30
20	40

11.4 Oxidation Reduction Potential (ORP) Calibration:

11.4.1 Ensure that meter reads 0.0mV when a shorting lead is placed on probe connector. Standard solution measurements made at stable temperature with an electrode that is functioning properly should be accurate to within +/- 10mV.

11.4.2 Place electrode in a beaker of Light's solution. While gently stirring, wait for reading to stabilize, this may take a few minutes. Record mV reading and temperature. Light's solution and samples should be at room temperature. The true value for Light's solution is 475 mV at 25°C. The ORP probe reading should be within 10mV of this true value. If it is not, the probe must be cleaned or replaced

12. Procedure

12.1 **Solid Digestion**.

12.1.1 Place 2.5g (+/- 0.10g) of the field-moist sample into a clean, labeled 150mL digestion vessel. The sample should be mixed thoroughly before taking an aliquot. Spike material should be added to the aliquots for matrix spikes at this point.

12.1.2 Soluble Spike Preparation: Add 2mL of the Stock Soluble Spiking Standard (50mg/L) to the sample aliquot for a spike concentration of 20mg/Kg.

12.1.3 Insoluble Spike Preparation: Add 12mg of the Stock Insoluble Spiking Standard to the sample aliquot for a spike concentration of 644-1288mg/Kg.

12.1.4 Post Digestion Spike: Remove 10 ml of sample from a digested sample and spike with 10 ml of 5 mg/L 2nd Source. TV= 20mg/kg.

12.1.5 Record the weight of spiking standard added to determine exact spike amount.

12.1.5.1 Use 2.5g of glass beads for the Method Blank, LCS/ICV and CCV sample.

12.1.5.2 Spike the LCS/ICV sample with 10mL of the 5mg/L secondary standard solution. The True Value is 20mg/kg.

12.1.5.3 Spike the CCV sample with 2mL of the 5mg/L primary standard solution. The True Value is 4mg/kg.

12.1.6 Add 50mL of digestion solution to each sample using a graduated cylinder and add approximately 400mg magnesium chloride. Also add 0.5mL of the 1M phosphate buffer to each sample. Cover all samples with watch glasses.

12.1.7 Prior to heating, stir the sample continuously for approximately 5 minutes. Heat the samples to 90-95 ºC and maintain that temperature for at least 60 minutes with continuous stirring.

12.1.8 Gradually cool each solution to room temperature. Transfer the contents of each vessel quantitatively to the filtration apparatus, by rinsing the digestion vessel with 3 successive portions of DI water and transferring the rinsates to the filtration apparatus.

12.1.9 Filter the samples through a 8µm membrane filter. Rinse the inside of the filter flask and filter pad with DI water and transfer the filtrate and the rinses to a clean 150mL vessel.

12.1.10 Caution**:** This step should be performed under a fume hood because of the formation of carbon dioxide fumes.

12.1.11 Place the sample digest beaker onto a magnetic stirrer and add a magnet to the beaker. With constant stirring, slowly add concentrated nitric acid solution to the beaker drop wise. Adjust the pH of the solution to 7.5 +/- 0.5 pH units (Method 7196A) and monitor the pH using the pH meter. If the pH of the digestate deviates from the desired range, discard the solution and redigest. If this occurs repeatedly, dilute the nitric acid solution and repeat the digestion.

12.1.12 Remove the stir bar and rinse it off into the beaker. Quantitatively transfer the contents of the beaker to a 100mL volumetric flask and adjust to the mark with DI water.

12.1.13 The sample digestates are now ready for analysis. Determine the chromium (VI) content by using EPA Method 7196A, SOP PGH-I-012, Hexavalent Chromium Analysis.

12.2 **Oxidation Reduction Potential (ORP) Procedure**:

12.2.1 Weigh 20g of soil sample into a glass beaker. Add 20mL reagent water.

12.2.2 While gently stirring the sample, submerge the end of the ORP electrode into the slurry so that the ion exchange junction is covered. Wait for the reading to stabilize.

12.2.3 Record the mV reading and the sample temperature. The temperature of the Light's solution and samples should not differ by more than 2°C, otherwise the mV correction may be inaccurate.

12.2.4 Rinse the probe with reagent water and repeat the measurement procedure to verify the initial reading.

12.2.5 Calculations

$$Eh_{system} = Eh_{observed} + (Eh_{reference\ standard} - Eh_{reference\ observed})$$

Where $Eh_{reference\ standard}$ = 475 for a silver:silver chloride electrode filled with 4M KCl and using the Light's solution at 25ºC.

$Eh_{reference\ observed}$ = Reading obtained during calibration with Light's solution.

Eh_{system} = final reading for the sample corrected for the deviation from the true and observed values for the calibration standard.

13. Calculations

13.1 Concentration of Cr^{+6} in Solid Samples:

$$[Cr^{+6}](mg/Kg) = \frac{[Abs_{ColoredSample} - Abs_{UncoloredSample}] - Intercept}{Slope} * DF * \left(\frac{0.1L}{SmplMass(Kg)}\right)$$

Where:
$Abs_{ColoredSample}$ = Absorbance of Sample after coloring
$Abs_{UncoloredSample}$ = Absorbance of Sample before coloring
DF = any dilutions performed

13.2 Sample Concentration = $\frac{A \times D \times E}{B \times C}$

Where: A = concentration observed in the digestate (ug/mL)
B = initial moist sample weight (g)
C = % solids/100
D = dilution factor (if applicable)
E = final digest volume (mL)

14. Quality Control

14.1 Table 14-1 Sample QC Requirements:

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Glass Beads	One (1) per batch of up to 20 samples.	a) Target analyte must be less than reporting limit or less than ½ the RL if required by the client. b) If results are reported to MDL, target analyte in MB should be non-detect.	Reanalyze the method blank once. If still out, re-digest and reanalyze the entire bacth if target compound is >RL in the method blank. ***Exceptions:*** 1) If a contaminant is present only in the method blank and not the samples, the sample data may be reported without qualifiers, the method blank must be qualified. 2) If sample result >10x MB level and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination.

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCS)	Cr (VI)	One (1) per batch of up to 20 samples.	% Rec within 80 – 120%.	1) Reanalyze the LCS first. If it is still outside the QC limit, re-digest and reanalyze associated samples if LCS is outside acceptance limits. 2) If problem persists, check the spike solution. 3) Perform system maintenance prior to new LCS analysis. ***Exceptions:*** 1) If the LCS recovery > QC limits and the results are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Cr (VI)	One **soluble MS** and one **insoluble MS** per preparation batch of up to 20 samples.	% Rec within 75 – 125%.	If outside acceptance limits, evaluate sample for pH and Eh and compare to Figure 2 from Method 3060A, Attachment 1. If in reducing range, no re-digestion is required. If outside reducing range, re-digestion and reanalysis of the entire preparation batch is required.[1]
Duplicate Sample (DUP)	Cr (VI)	One (1) per 20 environmental samples.	RPD ± 20%.	1) Reanalyze the duplicate sample *Exceptions:* 1) If sample ND, report sample without qualification 2) If the sample is just above the PRL and duplicate is just below the PRL, report data without qualifications.
Post Digestion Spike	Cr(VI) at 20mg/Kg or 2x sample conc.	One (1) per batch of up to 20 samples.	85-115% Recovery	No corrective actions necessary.

[1]A value of Eh-pH below the bold diagonal line on Fig. 2 indicates a reducing soil for Cr(VI). The downward slope to the right indicates that the Eh value, at which Cr(VI) is expected to be reduced, decreases with increasing pH. The solubility and quantity of organic constituents influence reduction of Cr(VI). The presence of H S or other strong odors 2 indicates a reducing environment for Cr(VI). In general, acidic conditions accelerate reduction of Cr(VI) in soils, and alkaline conditions tend to stabilize Cr(VI) against reduction. If pre-digestion matrix spike recovery is not within the recovery limits, the reductive nature of the sample must be documented. This is done by plotting the Eh and pH data on the EhpH diagram (Fig. 2) to see if spike recovery is or is not expected in the soil. If the data point falls below the Cr(VI)-Cr(III) line on the diagram, then the data is not qualified or rejected. The sample is reducing for Cr(VI). If the data point falls above the line, then the sample is capable of supporting Cr(VI). In this case, technical error may be responsible for the poor spike recovery, and the extraction should be repeated, along with the Eh and pH measurements. If re-extraction results in a poor spike recovery again, then the data is qualified.

15. Method Performance

15.1 If the method blank is above the reporting limit, check all glassware and reagents for contamination. If contamination is present, prepare new reagents and reanalyze all associated samples.

15.2 If the percent recovery for the LCS is not within the acceptance limits, reanalyze the LCS first. If it is still outside the QC limit, re-digest and reanalyze the entire batch associated with the LCS. If problem persists, check the spike solution. Also perform system maintenance prior to new LCS analysis. If the LCS recovery is greater than QC limits and the results are non-detect in the associated samples, report and qualify the sample data.

15.3 If the RPD for the duplicate is greater than 20% for solid or organic waste sample, reanalyze the sample duplicate, if it is still out report and qualify the data.

15.4 If the spike recoveries are not within the control limits specified in Table 14-1 for solid or organic waste samples, evaluate the data as per Table 14-1, Sample Quality Control requirements.

15.5 Any data that are considered out-of-control (suspect) or unacceptable will be appropriately flagged as such and qualified in the analytical report.

15.6 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.7 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.8 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.9 Solid MDL

	Soil		
LOQ	1.0mg/kg		
LOD	0.364mg/kg	Effective 11/19/14	LODs are subject to change

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

16.2 All wastes and samples must disposed of via the established laboratory waste stream(s). Samples that contain hexavalent chromium are considered hazardous.

17. References

17.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solids and Wastes, SW-846 Method 3060A, Revision 1, December 1996.

17.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solids and Wastes, SW-846 Method 7196A, Revision 1, July 1992.

17.3 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.4 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.5 Pace Analytical Services, Inc. – Pittsburgh Laboratory Quality Assurance Manual, current version.

17.6 PGH-I-012, Hexavalent Chromium Analysis, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No. 1 – eh/pH Phase Diagram, Method 3060A

18.2 Attachment No. 2 – Alkaline Digestion Logbook (Example)

19. Revisions

Document Number	Reason for Change	Date
PGH-I-066-0	Initial release of procedure.	21Apr2015
PGH-I-066-1	1. Updated Cover Page, Headers and Footers for this revision 2. Section 9.1: Changed spectrometer manufacturer to the current one being used., Section 9.15: Changed the ORP manufacturer to the current one being used. 3. Section 10.6 and 10.7: Diphenylcabazide solution updated to current practice (larger volume of solution), 0.2N sulfuric acid changed to 1:1 sulfuric acid to match process in lab.. Section 10.11: removed reference to phosphoric acid (not used), Section 10.12 clarified the use of 12mg of lead chromate for spikes (matches process in lab) Sections 10.13 and 10.14: Removed (not used in this procedure) Section 10.13 Added Zobel Solution to SOP (used to calibrate the ORP meter) 4. Section 12.1.3 changed to 12mg of lead chromate, Changed filter paper specification in Section 12.1.9 from 0.45um to 8um. (Whatman grade 2 specification), Section 12.10: Removed (not doing)	

20. Instrument and Equipment Maintenance

20.1 Replace the lamp on the spectrophotometer as needed. If the lamp is replaced; prepare a new calibration curve.

20.2 Record all maintenance in the maintenance logbook

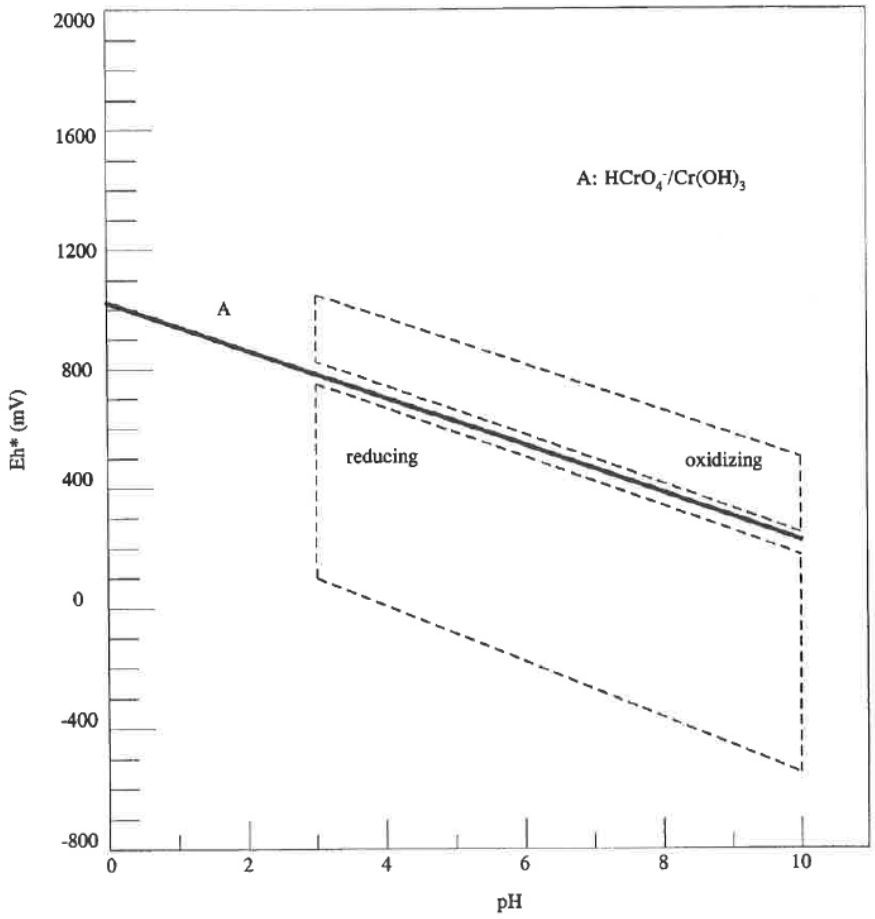
21. Method Modifications

21.1 Spikes have been adjusted to 20 mg/kg to fit within our curve.

Attachment No. 1 – eh/pH Phase Diagram, Method 3060A

FIGURE 2
Eh/pH PHASE DIAGRAM

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

Attachment No. 2 – Alkaline Digestion Logbook (Example)

Pace Analytical Services, Inc.-Pittsburgh

Solid Hexavalent Chromium Extraction Logbook

Logbook ID: 1-I007-3 Prep. Method: SW 846 3060A Analytical Method: SW 846 7196A
SOP ID: PGH-I-012

Analyst: _____

Heat Temp Limits: 90-95°C Set A/Start Time: _____ End Time: _____
Set B/Start Time: _____ End Time: _____

Balance ID: _____ Pipette ID : _____

Reagents

Cr+6 Digestion Sol. ID: _____ 0.4 g MgCl ID: _____
0.5 mL Buffer ID: _____ 1:1 H2SO4 ID: _____
Coloring Reagent ID: _____ pH Acceptable Limits 7.5 ± 0.5

Project #	Sample ID	Date	Sample Matrix	Sample Weight (g)	Digestion Set	pH	Comments

Peer Review: _____

STANDARD OPERATING PROCEDURE

Hexavalent Chromium Analysis

Methods: SW 846 7196A, SM 3500-Cr B-2009 & SM-3500-Cr D

SOP NUMBER:	PGH-I-012-10
REVIEW:	Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-012-9
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager — 07/06/15 Date

Senior Quality Manager — 07/06/15 Date

Department Manager/Supervisor — 07/06/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This SOP documents the procedure to be used for the analysis of hexavalent chromium (Cr^{+6}) per SW-846 Methods 7196A and Standard Method 3500-Cr B-2009 and 3500-Cr D. Soil sample preparation is described in the SOP PGH-I-066, Alkaline Digestion of Solid Samples for Hexavalent Chromium.

2. Scope and Application

2.1 This procedure determines the total concentration of hexavalent chromium in a range of 0.01mg/L to 1.0mg/L for aqueous samples. The aqueous reporting limit (RL) is 0.01mg/L.

2.2 This SOP applies to aqueous samples and domestic and industrial wastes (of an aqueous nature) provided that no interfering substances are known to be present. Method 7196A is also applicable to TCLP, SPLP, and ASTM leachates.

3. Summary of Method

3.1 A colorimetric method is used to determine hexavalent chromium in the resultant digest or in an aqueous sample. The sample is acidified and diphenylcarbazide is added. If hexavalent chromium is present, a red-violet color is produced. The concentration of hexavalent chromium is determined by measuring the absorbance of the sample at 540nm.

4. Interferences

4.1 Hexavalent molybdenum (Mo^{+6}) and mercury salts can interfere, but concentrations as high as 200 mg Mo or Hg/L can be tolerated.

4.2 Vanadium will interfere, but concentrations up to ten times that of Cr^{+6} can be tolerated.

4.3 Any permanganate (MnO_4^-) interference is dispelled by adding azide. Iron may produce a yellow color but it is not intense enough to interfere as long as the correct wavelength is used.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

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7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Sample collection: Samples should be collected and stored in plastic or glass containers (Do not use stainless steel containers or lids that are lined with stainless steel).

8.2 Preservation: Samples should be chilled to $4\pm2^{o}C$.

8.3 Shipment: Samples should be shipped in a cooler, chilled with ice to a temperature of $4\pm2^{o}C$.

8.4 Storage: Samples are to be stored at $4\pm2^{o}C$

8.5 Hold Times

8.5.1 Aqueous samples must be analyzed within 24 hours of sample collection.

8.5.2 Solid samples must be digested within 30 days of the collection date and digestates must be analyzed within 7 days of the digestion date.

9. Equipment and Supplies

9.1 Spectrophotometer set at 540 nanometers (Hach DR-5000 or equivalent).

9.2 1 centimeter (cm) absorption cell.

9.3 150mL beakers.

9.4 Funnels.

9.5 Filter paper (Fisher P4 or equivalent).

9.6 A volumetric flasks, 50mL, 100mL, 200mL, 1L Class A, glass.

9.7 Hot plate with stirrer.

9.8 Volumetric pipettes (assorted volume as necessary) or Class A.

9.9 Magnetic stir bars.

9.10 Watch glasses.

9.11 pH meter (Fisher AR-50, or equivalent).

9.12 Graduated cylinder, 100mL.

9.13 Analytical balance, accurate to 0.01g.

9.14 IPAQ (see IPAQ SOP for instructions).

10. Reagents and Standards

10.1 Acetone (Fisher Optima® grade or equivalent).

10.2 Primary Stock Chromium (Cr^{+6}) Solution (500mg/L): In a 100mL volumetric flask, dissolve 141.4mg potassium dichromate ($K_2Cr_2O_7$,ACS grade) in DI water and dilute to volume with DI water. This solution is good for a maximum of 6 months.

10.3 Secondary Stock Chromium (Cr^{+6}) Solution (500mg/L): In a 100mL volumetric flask, dissolve 141.4mg potassium dichromate ($K_2Cr_2O_7$) {from a source other than that used for the primary stock solution}(ACS grade) in DI water and dilute to volume with DI water. This solution is good for a maximum of 6 months.

10.4 Standard Cr^{+6} Working Solution(s): In a 250mL volumetric flask, dilute 2.5mL of the stock Cr^{+6} solution to volume with DI water (5mg/L) This solution is good for a maximum of 1 month. Prepare both a primary and secondary solution from the stocks listed above.

10.5 CCV 0.1 PPM: In a 150 ml beaker add 2 ml of the 5 mg/L primary source and 98 mls of DI water.

10.6 ICV and LCS 0.25 PPM: In a 150 ml beaker add 5 ml of the 5 mg/L secondary working solution and add 95 ml of DI water. ICV and LCS are the same standard.

10.7 Matrix Spike 0.25 PPM: In a 150 ml beaker add 5 ml of the 5 mg/L secondary working solution and add 95 ml of sample.

10.8 Diphenylcarbazide Solution: Dissolve 250mg 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide,ACS grade) in acetone and dilute to 50mL with acetone in a 50mL volumetric flask. Store in an amber bottle. Expires one week after preparation or if solution becomes discolored.

10.9 0.2N Sulfuric Acid: Dilute 40mL 1N H_2SO_4 (Fisher purchased solution or equivalent) with a 100mL graduated cylinder to 200mL with DI water in a 200mL volumetric flask.

10.10 Concentrated Nitric acid: Trace metal grade, or equivalent. If the Nitric Acid has a yellow color this is indicative of photoreduction of nitrate ions to nitrite, a reducing agent for Chromium VI. Do not use this acid.

10.11 Phosphoric acid, H_3PO_4, concentrated: Trace metal grade, or equivalent.

11. Calibration

11.1 A calibration curve for standard methods 3500-Cr B and 3500-Cr D must be analyzed at the beginning of each batch of samples and when calibration verification acceptance criteria are not met, when a new stock is made, or when a QC sample fails. A second source Laboratory Control Sample/ Initial Calibration Verification (LCS/ICV) must be

prepared made up to verify the initial calibration. For Method 7196A a calibration curve is good for 6 months unless the stock solution expires or the QC check standard fails.

11.2 Prepare the standards and a blank by pipetting suitable volumes of the 5mg/L Working Standard Solution into a 100mL volumetric flask and dilute to volume with DI water.

Volume of 5mg/L Working Standard (mL)	Concentration (mg/L)
0.2	0.01
0.5	0.025
1	0.05
2	0.10
5	0.25
10	0.50
15	0.75
20	1.00

11.3 Standards are analyzed and the absorbance values are recorded onto a benchsheet.

11.4 A standard curve is prepared by entering the absorbance values of the standards and the corresponding Cr^{+6} concentrations into the HEX-CHROME spreadsheet (See Attachment No.1). This spreadsheet performs a linear regression on the data and displays the regression statistics. The correlation coefficient (r) must be greater than or equal to 0.995.

11.5 A MBLK (method blank), LCS/ICV, CCV, matrix spike and a DUP must be run with each Batch. For soil sample QC refer to SOP PGH-I-066.

12. Procedure

12.1 Colorimetric Procedure 3500Cr-D

12.1.1 Turn on the spectrophotometer and set the absorbance at 540nm. Allow it to warm up for 15 minutes prior to use.

12.1.2 Measure out 100mL of the filtered sample into a graduated cylinder and transfer it to a clean 150mL beaker. Record the initial volume of the sample on the bench sheet under “SAMPLE VOL/WT”.

12.1.2.1 If the sample is extremely colored or turbid, it may be necessary to dilute it. Note any dilutions on the bench sheet.

12.1.3 Using the pH meter, adjust the pH of the sample to 1.0 ± 0.3 (for SM3500Cr-D) or to 2.0 ± 0.5 (for SM3500Cr-B) using 0.2N H_2SO_4. Document the pH adjustment on the bench sheet.

12.1.4 Take an absorbance reading of each sample prior to coloring and record this reading on the bench sheet under “BLANK READING”. This will be subtracted from the final absorbance.

12.1.5 Add 2.0mL diphenylcarbazide solution to the sample and mix. Allow color to develop for a minimum of 10 minutes.

12.1.6 The first sample read should be the method blank (MB). Zero the spectrophotometer on the method blank before reading the samples.

12.1.7 Transfer an appropriate amount of the sample to a 1cm absorption cell and measure the absorbance. Record the absorbance reading on the bench sheet under "SAMPLE ABSOR."

12.1.8 Any sample that has an absorbance greater than that of the high standard in the calibration curve must be diluted and reanalyzed.

12.1.9 Once all of the samples have been read, the information is transferred from the bench sheet to the computer spreadsheet which contains the most recent calibration curve or to the IPAQ. This spreadsheet calculates the final results. These results are then entered into the LIMS.

12.2 Colorimetric Procedure 3500Cr-B

12.2.1 For SM3500Cr-B – Add 0.25mL (5 drops) H_3PO_4 to the sample.

12.2.2 Same steps as in section 12.1 except for section 12.1.3. For this method in section 12.1.3 above use 0.2N H_2SO_4 and a pH meter to adjust solution to pH 2.0 ± 0.5. Document the pH adjustment on the bench sheet.

12.3 Colorimetric Method 7196A

12.3.1 For soil sample prep refer to SOP PGH-I-066.

12.3.2 Turn on the spectrophotometer and set the absorbance at 540nm. Allow it to warm up for 15 minutes prior to use.

12.3.3 Place 95 mL of sample or entire 100 ml of solid digestate into a beaker. If turbid or dark in color, dilute accordingly.

12.3.4 Add 1:1 H_2SO_4 until the sample pH is 2 ± 0.5. Document the pH adjustment on the bench sheet.

12.3.5 Take an absorbance reading of each sample prior to coloring and record this reading on the bench sheet under "BLANK READING". This will be subtracted from the final absorbance.

12.3.6 Add 2mL of Diphenylcarbazide coloring reagent and mix..

12.3.7 Allow sample stand for 5-10 minutes for color development.

12.3.8 Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method.

13. Calculations

13.1 Concentration of Cr^{+6} in Aqueous Samples:

$$[Cr^{+6}](mg/Kg) = \frac{[Abs_{ColoredSample} - Abs_{UncoloredSample}] - Intercept}{Slope} * DF * \left(\frac{0.1L}{SmplMass(Kg)}\right)$$

Where:
$Abs_{ColoredSample}$ =Absorbance of Sample after coloring
$Abs_{UncoloredSample}$ = Absorbance of Sample before coloring
DF = any dilutions performed

13.2 Sample Concentration = $\frac{A \times D \times E}{B \times C}$

Where: A = concentration observed in the digestate (ug/mL)

B = initial moist sample weight (g)
C = % solids/100
D = dilution factor (if applicable)
E = final digest volume (mL)

13.3 LCS equation:

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

13.4 MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

13.5 RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

14. Quality Control

14.1 QC Acceptance Criteria Table 14-1.

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water (DI)	One (1) per batch of up to 20 samples.	a) Target analyte must be less than reporting limit or less than ½ the RL if required by the client. b) If results are reported to MDL, target analyte in MB should be non-detect. .	Reanalyze the method blank once. If still out, re-digest and reanalyze the entire batch if target compound is >RL in the method blank. For soil sample prep refer to SOP PGH-I-066. ***Exceptions:*** 1) If a contaminant is present only in the method blank and not the samples, the sample data may be reported without qualifiers, the method blank must be qualified. 2) If sample result >10x MB level and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination.
Laboratory Control Sample (LCS)	Cr (VI)	One (1) per batch of up to 20 samples.	% Recovery within 85 - 115%.	1) Reanalyze the LCS first. If it is still outside the QC limit, re-digest and reanalyze associated samples if LCS is outside acceptance limits. (Only solid samples are digested.) 2) If problem persists, check the spike solution. 3) Perform system maintenance prior to new LCS analysis. ***Exceptions:*** 1) If the LCS recovery > QC limits and the results are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Cr (VI)	One (1) per batch of up to 10 samples.	[7196] % Recovery within 85 - 115%. [3500Cr B_D] % Recovery within 70 – 130%	1) If the LCS and MBs are acceptable, the spike results should be reviewed and it may be reported with appropriate footnote indicating matrix interferences. For solids samples refer to SOP PGH-I-066, method 3060A spike requirements. 2) [7196] If addition of the spike extends the concentration beyond the

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
				calibration curve, the sample should be diluted with blank solution and the calculated results adjusted accordingly. 3) [7196] If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. 4) [7196] See section 15.4 for additional requirements.
Duplicate Sample (DUP)	Cr (VI)	One (1) per batch of up to 10 samples.	RPD ± 20%.	1) Reanalyze the duplicate sample *Exceptions:* 1) If sample ND, report sample without qualification 2) If the sample is just above the PRL and duplicate is just below the PRL, report data without qualifications.
Initial Calibration Verification (ICV)	Cr (VI)	After initial calibration.	%Recovery 90 - 110%.	Reanalyze the ICV once. If it is still outside QC limits, perform system maintenance. Recalibrate the instrument and reanalyze the ICV.
Continuing Calibration Verification (CCV)	Cr (VI)	One every 15 samples.	% Recovery within 90 - 110%.	If CCV fails, re-analyze the CCV once. If it fails again, reanalyze all affected samples since the last acceptable CCV. If CCV fails again, recalibrate and reanalyze the associated samples since to the last acceptable CCV. Samples must be bracketed with acceptable CCVs.
Initial or Continuing Calibration Blank (ICB/CCB)	Reagent (DI) water	Before beginning a sample run, after every 10 samples, and end of the analysis sequence. ICB/CCB is analyzed after the ICV and CCVs.	Target analyte must be less than the reporting limit or 1/2 the reporting limit if required by client.	Reanalyze the CCB once. If it is still out, correct the problem and re-prep and reanalyze the CCB. All samples following the last acceptable calibration blank must be reanalyzed. Samples must be bracketed by acceptable CCBs.

15. Method Performance

15.1 If the method blank is above the reporting limit, check all glassware and reagents for contamination. If contamination is present, prepare new reagents and reprepare and reanalyze all associated samples. Refer to Table 14-1 for corrective action criteria.

15.2 If the percent recovery for the ICV is not within the acceptance limits (Table 14-1), a new calibration curve may be needed. Refer to Table 14-1 for corrective action criteria.

15.3 If the RPD for the duplicate is greater than 20%, reanalyze the duplicate sample. See Table 14-1. Refer to Table 14-1 for ICB/CCB, LCS and MS and duplicate corrective action criteria.

15.4 If the spike recovery is not within 15%, evaluate the LCS sample. If the LCS is within range, matrix interferences are suspected and must be indicated on the bench sheet and in the final report. If the spike result indicates a suppressive interference, the sample should be diluted and reanalyzed. If there is persistent interference this indicates the need to use alternative method. Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

15.5 Any data that are considered out-of-control (suspect) or unacceptable will be appropriately flagged as such and qualified in the analytical report.

15.6 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.7 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.8 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Aqueous LOD/LOQ

	Water		
LOQ	0.01mg/L		
LOD	0.00394mg/L	Effective 12/05/14	LODs are subject to change

17. Pollution Prevention and Waste Management

17.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

17.2 All wastes and samples must disposed of via the established laboratory waste stream(s). Samples that contain hexavalent chromium are considered hazardous.

18. References

18.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solids and Wastes, SW-846 Method 7196A, Revision 1, July 1992.

18.2 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 19th Edition, Method 3500-Cr D. pp.3-59&3-60, United Book Press, Inc., Baltimore, Maryland, 1995.

18.3 Standard Methods for the Examination of Water and Wastewater, Method 3500-Cr B-2009, Hexavalent Chromium Colorimetric Method, Approved by Standard Methods Committee.

18.4 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

18.5 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

18.6 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18.7 PGH-I-066, Alkaline Digestion of Solid Samples for Hexavalent Chromium, current version.

19. Tables, Diagrams, Flowcharts, Appendices, etc.

19.1 Attachment No. 1 – Hex-Chrome-Spec 21 Bench Sheet (Example)

20. Revisions

Document Number	Reason for Change	Date
PGH-I-012-7	1. Added Section 11.5: The solid calibration curve is made up of the same curve points except for the 0.01 ppm standard. The curve is digested following the same procedure as the samples using 2.5g of glass beads.	03/04/14
PGH-I-012-8	1. Cover and Sections 1.1 and 18.6: updated method reference to latest MUR. 2. Section 2.2: Added statement regarding applicability of leachates. 3. General: made editorial corrections. 4. Document Reformatted.	31May2014
PGH-I-012-8	1. Removed solid digestion method 3060A and added to its own SOP PGH-I-066. Updated table in section 14.1 to be consistent with SOP PGH-I-066 and method 7196A. Updated references. Added QC calculation formulas. Updated sections 12.2.1, 12.3.4 and 12.3.5. Added section 10.5-10.7. LOD updated. 2. Added to section 15.4: Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.	24Apr2015
PGH-I-012-10	1. Updated cover page, headers and footers for this revision 2. Section 8.5 – Added time information for solid samples because this procedure is used for the analysis of the digestates. 3. Section 11.1 - changed frequence of ICAL from every 6mo to prior to each batch of samples for SM 3500-Cr B &D.	06Jul2015

Document Number	Reason for Change	Date
	Section 14.1 - Clarified MS acceptance limits for 7196 and 3500Cr B & D in the table.	

21. Instrument and Equipment Maintenance

21.1 Replace the lamp on the spectrophotometer as needed. If the lamp is replaced; prepare a new calibration curve.

21.2 Record all maintenance in the maintenance logbook

22. Method Modifications

22.1 A CCV standard is analyzed to verify the calibration at the beginning and end of the sequence.

Attachment No. 1 - Hexavalent Chromium - Bench Sheet (Example)

Pace Analytical™
PITTSBURGH, PA

BENCHSHEET

TEST: Hex-Chrome (Aqueous)
ANALYST:
START TIME: 05/26/2011 17:36:51
END TIME: NONE
INSTRUMENT: Milton-Roy 21D (30WET2)
BENCHSHEET: 1CR6A05262011.HTML
BATCH:
HBN:

REAGENT LIST

COLOR REAGENT: wc4-119-10
CCV: wc4-145-09
LCS 303373: wc4-145-08

Validated by DLH on 5/31/11

Type	Sample ID	PROCCODE	BLANK	ABSORB	Initial (mL)	Final (mL)	Dil. Fact.	Raw Conc. (mg/L)	Final Conc. (mg/L)
CCV	CHECK	3500CrDW		0.082	100	100	1	0.0992	0.0992
BLANK	[redacted]	3500CrDW		-0.004	100	100	1	-0.0023	-0.0023
LCS	[redacted]	3500CrDW		0.201	100	100	1	0.2397	0.2397
PS	[redacted]	3500CrDW	-0.002	-0.001	100	100	1	0.0036	0.0036
DUP	[redacted]	3500CrDW	-0.001	-0.002	100	100	1	0.0013	0.0013
BLANK	CHECK	3500CrDW		-0.004	100	100	1	-0.0023	-0.0023
CCV	CHECK	3500CrDW		0.082	100	100	1	0.0992	0.0992
LCS	CHECK	3500CrDW		0.201	100	100	1	0.2397	0.2397

DUP Sample 303374 Original Sample: 3047328001

CURVE INFORMATION

CURVE DATE:	04/14/2011
ANALYST:	[redacted]

mg/L	Absorb.
0.01	0.006
0.025	0.019
0.05	0.04
0.1	0.082
0.25	0.21
0.5	0.425
0.75	0.631

R2 Value:	0.999947

RECOVERY

Type:	CCV
Sample ID:	CHECK
Value:	0.0992
True Value:	0.1
% Recovery:	99.2

RECOVERY

Type:	LCS
Sample ID:	[redacted]
Value:	0.2397
True Value:	0.25
% Recovery:	95.88

RPD

Type:	DUP
Sample ID:	[redacted]
Value:	0.0013
Original ID:	3047328001
Value:	0.0036
% RPD:	93.8776

RECOVERY

Type:	CCV
Sample ID:	CHECK
Value:	0.0992
True Value:	0.1
% Recovery:	99.2

RECOVERY

Type:	LCS
Sample ID:	CHECK
Value:	0.2397
True Value:	0.25
% Recovery:	95.88

STANDARD OPERATING PROCEDURE

Gravimetric Determination of Oil and Grease in Water
by Automated Solid Phase Extraction, Method 1664A

SOP NUMBER: PGH-I-042-8

REVIEW: Brayan Hampton

EFFECTIVE DATE: Date of Final Signature

SUPERSEDES: PGH-I-042-7

REVIEW DATE: Upon Procedural Change

APPROVALS

Marla L. Krutz
Assistant General Manager — 10/16/14 Date

Maureen K. DeRubeis
Senior Quality Manager — 09/30/14 Date

Department Manager/Supervisor — 10/14/14 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

SECTION **PAGE**

1. Purpose

1.1 This procedure describes the gravimetric determination of oil and grease and total petroleum hydrocarbon in aqueous matrices using automated solid phase extraction by EPA Method 1664A.

2. Scope and Application

2.1 This procedure is used to determination the n-hexane extractable material (HEM) and n-hexane extractable material that is not adsorbed by silica gel (SGT-HEM) in surface and saline waters and industrial and domestic aqueous wastes. Extractable materials that may be determined are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials. The method is based on prior Environmental Protection Agency (EPA) and association methods for determination of "oil and grease" and "total petroleum hydrocarbons" (TPH).

2.2 This procedure is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act. "Oil and grease" is a conventional pollutant defined in the Act and codified in40 CFR 401.16. The term "n-hexane extractable material" (HEM) reflects that this method can be applied to materials other than oils and greases. Similarly, the term "silica gel treated n-hexane extractable material" (SGT-HEM) reflects that this method can be applied to materials other than aliphatic petroleum hydrocarbons that are not adsorbed by silica gel.

2.3 This procedure is not applicable to measurement of materials that volatilize at temperatures below approximately 85ºC. Petroleum fuels from gasoline through fuel oil #2 may be partially lost in the solvent removal operation.

2.4 Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-hexane. Accordingly, recoveries of these materials may be low.

2.5 This procedure is capable of measuring HEM and SGT-HEM in the range of 5 to 1000 mg/L, and may be extended to higher levels by analysis of a smaller sample volume collected separately.

2.6 The reporting limit is 5.0mg/L for HEM and SGT-HEM.

3. Summary of Method

3.1 A 1L sample is acidified to pH 2.0 with a 1:1 solution of HCl: DI water and is extracted with an automated extractor system by passing the sample through a solid phase extraction (SPE) disk and eluting the analytes from the disk with n-hexane.

3.2 The n-hexane layer of the collected extract is transferred to an aluminum evaporation dish and evaporated using an evaporator.

3.3 The residue is weighed and reported as mg/L HEM.

3.4 The residue for the HEM determination may be re-dissolved in n-hexane and treated with silica gel for the SGT-HEM determination.

4. Interferences

4.1 Interferences that affect results may come from solvents, reagents, glassware, and other sample processing hardware.

4.2 Silica gel has the potential to inflate results for SGT-HEM if it is transferred with the hexane into the pan for the gravimetric determination.

4.3 Complex sample matrices may contain substances (such as particulate and detergents) that may interfere with the extraction procedure.

4.4 Samples containing high sulfur content may pose an interference problem because of the solubility of sulfur in n-hexane.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this procedure has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.

5.2 n-Hexane has been shown to have increased neurotoxic effects over other hexanes and some other solvents. Inhalation of n-hexane should be minimized by performing all operations with n-hexane in a hood or well-ventilated area.

5.3 n-Hexane is extremely flammable.

5.4 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

5.4.1 Any questions or concerns regarding safety of the information on the SDS sheets are to be referred to the Laboratory Safety Officer.

5.5 Caution: When making dilutions of acids, always add the acid slowly to the water with constant stirring. NEVER add water to acid.

5.6 Refer to the Pace Analytical Services, Inc. (PASI) – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.7 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.8 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 HEM (n-Hexane Extractable Material:) refers to material (Oil and Grease) extracted from the sample using n-hexane. Such substances could include relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related mater.

6.2 SGT-HEM (Silica Gel Treated n-Hexane Extractable Material) refers to components of HEM that are not absorbed by silica gel, commonly referred to at total petroleum hydrocarbons.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Collect approximately 1L of representative sample in a glass bottle, following conventional sampling practices, except that the bottle must not be pre- rinsed with sample before collection. To allow for potential QC failures, it is recommended that additional sample aliquots be collected.

8.1.1 If analysis is to be delayed for more than a few hours, adjust the sample pH < 2 with HCl or H_2SO_4 at the time of collection, and refrigerate at 0-4ºC (40 CFR 136, Table II). To establish the volume of HCl or H_2SO_4 required, collect a separate aliquot, adjust the pH of this aliquot to less than 2 with acid, and add the volume of acid determined to each sample bottle prior to collection. The pH is taken using a glass stirring rod or Pasteur pipette and pH paper. A clean Pasteur pipette or glass rod is used to take a small aliquot of sample for pH verification. This pipette or glass rod is retained during the SPE procedure and is rinsed onto the SPE disk with n-hexane during the hexane extraction step to include any residue that may have adhered to the pipette into the final sample extract.

8.1.2 If a sample is known or suspected to contain greater than 500mg/L of extractable material, a proportionately smaller volume of sample (the volume required will depend upon the estimated amount of extractable material) may be collected in a glass bottle. Add a proportionately smaller amount of HCl or H_2SO_4 solution to the smaller sample if preservation is necessary.

8.2 The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. Therefore, samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged.

8.3 All samples must be refrigerated at 4^oC from the time of collection until extraction (40 CFR 136, Table II).

8.4 All samples must be analyzed within 28 days of the date and time of collection (40 CFR 136, Table II).

9. Equipment and Supplies

9.1 Horizon SPE-DEX 3000XL Automated Extractor System, or equivalent.

9.2 Horizon Speed Vap. II 9000 Solvent Evaporation System, or equivalent.

9.3 Analytical balance capable of weighing to 0.1mg.

9.4 Oil and Grease Extraction Disks (SPE Disks) - 47mm or 90 mm, Pacific brand, or equivalent.

9.5 1L amber glass bottles 33 X 400-mm, or any of the following bottle sizes can be used with the appropriate cap adapter: 70 X 400, 89 X 400, 53 X 400, 58 X 400, 48 X 400, 63 X 400, 83 X 400 mm, and I-Chem 33 X 430 mm bottles, or equivalent.

9.6 Bottle cap adapters (if required). The water inlet valves for the SPE-DEX3000 XL and 1000 XL are designed to fit a 33 x 400-mm Boston Round Bottle. Wide mouth bottles and jars will require cap adapters.

9.7 An in-house vacuum system that is capable of maintaining a minimum of 13” of Hg at 1 standard cubic feet per min.

9.8 A nitrogen gas (dry N_2) source (or any inert gas source).

9.9 40mL VOA vials, unpreserved, for 47mm disks.

9.10 Adapter for 40mL VOA vials with a 19/22-connection end.

9.11 125mL Erlenmeyer flask, 19/22 standard taper, for 90mm disks.

9.12 125mL separatory funnel, 19/22 standard taper, for 90mm disks.

9.13 70mm and 105mm aluminum weighing pans, for the 47mm and 90mm disks, respectively.

9.14 5mL and 10mL Class A pipettes.

9.15 Disposable glass pipettes.

9.16 2mg and 1000mg Class S weight.

9.17 Desiccator

10. Reagents and Standards

10.1 n-Hexane, ACS Reagent Grade : 85% minimum purity, 99.0% min. saturated C6 isomers, residue less than 1mg/L.

10.2 Methanol, ACS Reagent Grade.

10.3 Silica Gel : anhydrous, 75-150µm, dried at 200 - 250° C for 24 hr minimum and stored in a desiccator or tightly sealed container.

10.4 1664A Oil & Grease standard, 2 sources required such as Horizon, containing 4mg/mL hexadecane and 4mg/mL stearic acid and Environmental Express, containing 2mg/mL hexadecane and 2mg/mL stearic acid. Stearic acid has a shelf life or five years. Hexadecane has a two year shelf life.

10.5 1:1 HCl: - DI H_2O Mix equal volumes of concentrated hydrochloric acid (ACS grade or better) and deionized (DI) water.

10.6 Blue food coloring or methylene blue solution – dissolve 0.05g methylene blue in 500mL deionized water.

11. Calibration

11.1 The calibration of the analytical balance must be verified with 2mg and 1000mg Class S weights prior to and at the conclusion of the mass determinations of the HEM sample analysis. Calibration shall be within ±10% (i.e., ± 0.2 mg) at 2mg and ± 0.5 % (i.e., ± 5 mg) at 1000mg. If values are not within these limits, recalibrate the balance. The balance is also checked to make sure that it is clean and level.

11.2 The balance calibration is verified each day of use. The balance verification must be repeated after the samples have all been weighed back.

12. Procedure

12.1 Sample preparation

12.1.1 Allow the samples to warm to room temperature.

12.1.2 Acidify the samples to a pH of 2.0 with 1:1 HCl: DI H_2O, if not already acidified.

12.1.2.1 DO NOT over acidify the samples, as this will cause the disk material to break down and result in low recoveries. Cap and invert the sample bottle several times to mix.

12.1.3 Mark the sample level on the outside of each bottle using a permanent marker. The sample volume will later be measured and used in the calculation of the oil and grease concentration.

12.1.4 Prepare 2 blank bottles by adding 950mL of reagent water to a bottle. Adjust the pH to 2.0 using 1:1 solution of HC: DI H_2O.

12.1.4.1 DO NOT over acidify. Invert the bottle several times to mix.

12.1.3.1. Pipette 5mL of the Horizon standard (or 10mL Environmental Express) using a Class A pipette into one of the blank bottles. The standards must be at room temperature for preparation.

12.1.3.2. Touching the tip of the pipette to the inside of the neck of the bottle, allow the standard to slowly and gently flow down the side of the bottle and to settle on the water layer. A cloudy precipitate will form on the water. Avoid automatic pipettes, which may shoot the standard into the water, introducing it

too quickly. If the standard is not properly floated, it can cause flow problems during the sample processing step.

12.1.3.3. DO NOT shake the bottle.

12.1.5 Attach a closed Water Sample Inlet Valve to each bottle. Use an adapter if necessary.

12.1.6 The standard, samples and blank are now ready for processing.

12.2 Instrument Startup Procedure

12.2.1 If using the system for the first time or if the system has not been used for an extended period of time, verify that the system has been properly installed and that all connections are properly in place. Refer to the operator manual for installation instructions.

12.2.2 Empty all waste recovery bottles (water and solvent) if necessary.

12.2.3 Fill the solvent bottles with appropriate solvents as follows:

- Prewet 1 connected to Prewet Fitting #1 on Extractor: n-hexane
- Prewet 2 connected to Prewet Fitting #2 on Extractor: methanol
- Rinse 1 connected to Rinse Fitting #1 on Extractor: methanol
- Rinse 2 connected to Rinse Fitting #2 on Extractor: n-hexane

12.2.3.1 Secure the caps on the solvent bottles. Loss of pressure in the bottles will occur if the caps are loose.

12.2.4 Turn on the main power switch on the back of the Controller and allow the Liquid Level Sensor(s) to stabilize for 3 to 5 minutes.

12.2.5 Turn on the gas source and slowly increase the main gas source pressure while checking for liquid and gas leak. Adjust the main gas source pressure in increments checking for leaks as the pressure is increased to a minimum of 60 psi and a maximum of 80 psi.

12.2.6 Turn on the in-house vacuum system and check for leaks.

12.2.7 Verify that there are no crimped lines that may impede the flow of liquids, gas, and vacuum.

12.2.8 Free the Elute Check valve(s) using the Check Valve Release Tool (P/N 02-0725).

12.2.8.1 In the center of the platform, below the drain hole, locate the Sample Collect Check Valve. Gently insert the needle end of the tool straight down into the opening and tap the head several times to free the check valve. This will move the Check Valve Ball off of the seat assembly. An internal spring will gently push the ball back into the sealing position. Refer to Appendix C of the Horizon Standard Operating Procedure for the Gravimetric Determination of Oil and Grease in Water Using Automated Solid Phase Extraction.

12.2.9 Place the Disk Holder Base onto the platform, lift and move the Liquid Sensor / Prewet Arm into the Disk Holder Base.

12.2.10 Place the collection vessel in position on the Taper of the unit by lifting and twisting to ensure a vacuum tight seal. An adapter is not required for an Erlenmeyer flask or separatory funnel with a standard taper19/22 fitting; however for a VOA vial, an adapter must be attached before it can be fitted to the taper.

12.2.11 Lower the Water Sample Bottle Arm.

12.2.12 Attach an empty sample bottle to the Water Sample Inlet Valve and place the valve into position on the Water Sample Bottle Arm.

12.2.13 A Purge sequence is initiated to remove any air from the solvent lines and to wash the parts of the extractor. This is also a good way to verify that the system is installed correctly and operating properly. The Purge sequence performs much like an actual extraction method by introducing the selected prewet and rinse solvents. Press the STATUS key to display the status for all three stations.

12.2.14 Select Station # 1 by pressing the A-key. Press the DRAIN function key (E-key). Then press the PURGE key (D-key). Press the A-key for YES to begin the purge on Station # 1. Follow the same procedure for Stations # 2 & 3 if using the 3000 XL extractor system. Run the purge sequence three times to ensure all air has been removed from the lines when first installed or when refilling the solvent bottles.

12.2.15 If the system is being used for the first time or has not been used for an extended period of time, create a method (refer to the operator manual on instructions for creating a new method) for a test run using 500mL DI water, no disk or screen, 47mm size Disk Holder Assembly, and the following conditions:

Methanol Prewet:	5 sec Dispense 1 sec Saturate 10 sec Soak 0 sec Drain
Air Dry:	10 sec
Methanol Discard :	2sec Dispense 20 sec Soak 1 min Elute

12.2.16 Remove the empty sample bottle(s) and collection vessel(s). Lift the Liquid Sensor/Prewet Arm(s) and place it outside the Disk Holder Base(s). Remove the Disk Holder Base from the platform.

12.3 Extraction Procedure (Note: n-Hexane is the extraction solvent. Methanol is used to prewet the filter. All methanol goes directly to waste.

12.3.1 Attach the Water Sample Inlet Valve(s) to the sample bottle(s). Use an adapter if required

12.3.2 Place the screen in the Disk Holder Base. Place the SPE disk on the screen. Use a 90mm Disk Holder and disk if processing dirty samples.

12.3.3 Insert the Riser into the Disk Holder Base over the disk. The Riser holds the disk in place. Screw on the aluminum Locking Ring, load the Disk Holder assembly onto the Extractor platform and place the Liquid Sensor / Prewet Arm in the Disk Holder Assembly. Load the Disk Holder Assembly on each station being used.

12.3.4 Label a collection vessel with the sample number and add a couple drops of dye to it.

12.3.4.1 Use 40mL VOA vials if using 47mm disks. If using VOA vials, attach the glass adapter to the vessel by screwing it on using

the turquoise cap. Do not screw on the adapter by using the glass part; this may not produce a good seal.

12.3.4.2 Use 125mL flasks or separatory funnel if using 90mm disks for dirty samples. An adapter is not necessary for the flasks or separatory funnel.

12.3.5 Place the collection vessel into position by lifting and twisting to ensure a vacuum tight seal.

12.3.6 Lower the Sample Holder Arm on the extractor unit for each station used.

12.3.7 Load the sample bottles onto the unit. Minimize the agitation of the standard (Refer to Section 12.1.3.1for Standard Preparation). With the Water Sample Inlet Valve aluminum shaft facing you, place your right index finger over the solvent rod on the right-hand side. This will prevent the sample from leaking out. Gently invert the bottle and place it onto the Holder Arm of the unit. Help guide the Water Sample Inlet Valve shaft onto the actuator key. Firmly press the valve in place.

12.3.8 Select the appropriate method for the extraction process according to the disk size and type (refer to the Factory Preset Methods guide in Appendix F of the Horizon Standard Operating Procedure for the Gravimetric Determination of Oil and Grease in Water Using Automated Solid Phase Extraction.). From the STATUS mode, select the station with sample loaded for processing by pressing the appropriate key. Press the A-key to increase the method number or the B-key to decrease the method number to the one desired.

12.3.9 Return to the STATUS mode and proceed as in Section 12.3.8 to load the method to each station being used.

12.3.10 Return to the STATUS screen and confirm that the stations are set to the desired method.

12.3.11 Press the E-key to run all stations. If running only one station, select the station by pressing the appropriate key and then press the A-key to start the extraction. Confirm the start of the extraction by pressing the A-key again.

12.4 Gravimetric determination:

12.4.1 Turn on the Speed-Vap II 9000 using the switch located on the back of the unit. Set the temperature of the Speed-Vap II 9000 between 35 °C and 45 °C. When using a high temperature setting (50 °C or above) the pan must be removed from the unit as soon as evaporation is complete. If left longer, some volatile components will be lost and result in poor recoveries.

12.4.2 Pre-weigh clean the aluminum pans using a calibrated analytical balance and record the initial weights on the bench sheet. Place the pans in the Speed-Vap II 9000 system.

12.4.3 Transfer the top n-hexane layer (clear) using a disposable glass pipette into the pre-weighed aluminum pan already in the Speed-Vap. Use tweezers or gloves when handling the aluminum pan to avoid adding moisture or oil from the fingers. Be careful not to transfer the blue layer.

12.4.4 Once the n-hexane has been transferred, RINSE THE SIDES OF THE COLLECTION VESSEL THREE TIMES using small volumes of clean

n-hexane. Transfer each rinse to the pre-weighed pan. Repeat for each sample extracted.

12.4.5 Close the Speed-Vap cover. Turn the VACUUM knob of Speed-Vap system to the ON position. Observe the swirling action of the solvent in the pans. Adjust the vacuum so that there is a gentle “swirling” or agitation” of the extract. If the “swirling” is too aggressive, splashing may occur along with the loss of volatile components.

12.4.6 Remove the aluminum pans when evaporation is complete. Place pans into the desiccator for 1hr, before taking the first gravimetric reading.

12.4.7 Assure that the balance verification has been completed prior to any mass determinations.

12.4.8 Weigh the pan with the residue to the nearest 0.1mg. Record the mass on the bench sheet.

12.4.9 Return the aluminum weighing pans to the Speed-Vap and briefly continue the evaporation process. The sample is being heated in this step on the Speed-Vap. Caution: Prolonged exposure to the evaporation process in the Speed-Vap can result in loss of the lower boiling HEM constituents. Return the pans back into the desiccator for 1hr before final weighing.

12.4.10 Re-weigh the pan and residue to the nearest 0.1mg. Record the mass on the benchsheet.

12.4.10.1 Repeat the process until there is less than a 4% or 0.0005g difference (whichever is less) between the two masses.

12.4.11 The balance verification must be repeated after the samples have all been weighed back.

12.5 Shut-down procedure for extractors:

12.5.1 Remove the Disk Holder Assembly(s) from the extractor unit, disassemble, and discard the used disks.

12.5.2 Place the Disk Holder at each station, and fill with warm water. Attach an Erlenmeyer flask. Select the station from the STATUS mode. Press the DRAIN (E-key) function and then the ELUTE (C-key). Repeat for each station. This procedure will remove any residual solvent from the check valve.

12.5.3 Turn off the vacuum pump and vent by removing the line attached to the waste bottle.

12.5.4 Turn off the gas supply.

12.5.5 Turn off the controller power.

12.5.6 Flush the Water Sample Inlet Valves by manually turning them open and closed while flushing under warm running water. Non-surfactant soap may be used to clean the valves. Make sure to thoroughly rinse them out. Do not scrub using a cleaning brush.

12.5.7 Leave the Water Sample Inlet Valves in a half open position to allow the water to drain.

12.6 SGT-HEM Determination

12.6.1 To ensure that the capacity of silica gel will not be exceeded, the amount of HEM must be less than 100mg or, if above 100mg, the

approximate value must be known. It is presumed that 3g will normally adsorb 100mg of all absorbable materials. Use a proportionate amount of silica for HEM above 100mg up to a maximum of 30g for 1000mg HEM.

12.6.2 Prior to use, a portion of the dried silica gel must be rinsed with n-hexane to remove SGT-HEM interferences. The filter used to n-hexane rinse the silica gel must be rinsed with n-hexane prior to filtration.

12.6.3 Add a small aliquot of n-hexane to the pan to redissolve the HEM. Warm the solution if necessary in the Speed Vap 9000.

12.6.4 Transfer the extract to a clean collection vessel containing 3.0g +0.3g of treated silica gel for every 100mg of HEM. Add a small, solvent rinsed stir bar to the collection vessel.

12.6.5 Repeat steps 12.6.3 and 12.6.4 several times to ensure that all residue has been redissolved. Add each n-hexane rinse to the collection vessel containing the silica gel.

12.6.6 Stir the collection vessel for 5 minutes on a magnetic stir plate.

12.6.7 Allow the silica gel to settle, and then filter through n-hexane rinsed filter paper into a clean collection vessel, rinsing several times with hexane.

12.6.8 Use a disposable polyethylene pipette to transfer the solution to a pre-weighed aluminum pan in the Speed Vap 9000 with three n-hexane rinses.

12.6.9 Evaporate the n-hexane and weigh the pan with the residue to the nearest 0.1 mg. Record the result on the bench sheet.

12.6.9.1 Follow the same procedures for balance verifications and constant mass determinations as listed for the HEM (Oil and Grease) portion of this SOP (Section 12.4).

12.6.10 Determine the mass of SGT-HEM by subtracting the tare weight from the total mass.

13. Calculations

13.1 Definitions:

13.1.1 W_1 = mass of the empty aluminum pan (mg)

13.1.2 W_2 = mass of the aluminum pan and the extraction residue(mg)

13.1.3 V_s = volume of the original sample (L)

13.1.4 C_P = concentration of polar material

13.1.5 C_T = HEM (Total Oil and Grease)

13.1.6 C_{NP} is the Concentration of non-polar material (SGT-HEM)

13.2 Calculate the concentration of HEM content from the samples as follows:

$$HEM\ (mg/L) = \frac{(W_2 - W_1)}{V_s}$$

13.3 Calculate the concentration of SGT-HEM (non-polar material) content from the samples as follows:

$$SGT\text{-}HEM\ (mg/L) = \frac{(W_2 - W_1)}{V_s}$$

13.4 Calculate the concentration of the polar material as follows:

$$C_P = C_T - C_{NP}$$

14. Quality Control

14.1 The following Quality Control samples must be analyzed with each batch of 20 samples (maximum) or on each day of analysis (whichever is more frequent):

14.1.1 Method Blank (MB) – An aliquot of DI water that is processed in the same manner as the samples within the batch.

14.1.1.1 Oil and Grease results for the method blank must be less than the detection limit.

14.1.1.2 If the acceptance range for the blank is not achieved, evaluate the results for the cause and correct. Re-extract and re-analyze all of the samples in the batch if enough sample is available.

14.1.1.3 Clearly flag and qualify any result(s) in the final report that are not associated with an acceptable method blank.

14.1.2 Laboratory Control Sample (LCS) - An aliquot of DI water that has been spiked with a known amount of the target analyte.

14.1.1.4 HEM Recovery must be within the range of 78-114%, and the SGT-HEM recovery must be within the range of 64%-132%. (Manufacturer's recommended limit).

14.1.1.5 If the acceptance range for the LCS is not achieved, evaluate the results for the cause and correct. Re-extract and re-analyze all of the samples in the batch if enough sample is available.

14.1.1.6 Clearly flag and qualify any result(s) in the final report that are not associated with an acceptable LCS.

14.1.3 Matrix Spike/Matrix Spike Duplicate Sample (MS/MSD) - An aliquot of client sample that has been spiked with a known amount of the target analyte. One matrix spike per 20 samples is required.

14.1.1.7 HEM Recovery must be within the range of 78-114% and relative percent difference of less than 18%, and the SGT-HEM recovery must be within the range of 64%-132% with a relative percent difference of less than 34%. (Manufacturer's recommended limit).

14.1.1.8 If the acceptance ranges for the MS/MSDs are not achieved, evaluate the results for the cause and correct. Re-extract and re-analyze the samples in the batch if enough sample is available.

14.1.1.9 Clearly flag and qualify any result(s) in the final report that are not associated with an acceptable MS/MSD.

14.2 Corrective Actions for Out-Of-Control Data

14.2.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.2.2 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are noted in the final report.

14.2.2.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.2.3 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.2.4 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.2.4.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.2.5 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 Oil and Grease 1664A method performance is achieved through the analysis of MDLs , semi-annual performance evaluations, and in house laboratory control samples.

15.2 The method detection limit (MDL) is determined as specified by program or client requirements, and must meet the criteria as set forth in 40 CFR part 136 Appendix B and in the Pace Analytical Services, Inc. SOP for MDLs. MDL must also meet method requirement of 1.4mg/L.

15.3 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.4 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.5 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.6 LOD/LOQ

LOQ	5.0mg/L		
LOD	1.22mg/L	Effective 3/31/14	LOD is subject to change.

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and the specific reagent spilled. Specific protocols for handling spills are found in the Pace Analytical Health and Safety Policy Manual and in the SDSs

17. References

17.1 Horizon Technology, "Standard Operating Procedure for the Gravimetric Determination of Oil and Grease in Water Using Automated Solid Phase Extraction," Rev. 12/09/02.

17.2 USEPA, Method 1664, Revision A, "n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry," EPA-821-R-98-002, Feb 1999.

17.3 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.4 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.5 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No. 1: Oil & Grease Bench Sheet (Example).

19. Revisions

Document Number	Reason for Change	Date
PGH-I-042-5	1. Added Section 8.1.1, The pH is taken using a disposable glass stirring rod and pH paper. 2. Section 9.15 added disposable glass pipette. 3. Section 12.4.6 added: Place pans into the desiccator for 1hr. before taking the first reading 4. Added to section 12.4.9: Sample is being heated in this step on the Speed-Vap. Return the pans back into the desiccator for 1hr. before final reading. 5. Added to section 14.1.3: One matrix spike per 20 samples is required. 6. Section 15.3 LOD and LOQ added.	03Apr2013
PGH-I-042-6	1. Weights added to Section 9, Equipment and Supplies. 2. Weights added to Section 11, Scale calibration. 3. Section 8.1.1 added: A clean Pasteur pipette or glass rod is used to take a small aliquot of sample for pH verification. This pipette or glass rod is retained during the SPE procedure and is rinsed onto the SPE disk with hexane during the hexane extraction step to include any residue that may have adhered to the pipette into the final sample extract. The glass rod is then rinsed with n-hexane that is used for the extraction. 4. Updated references.	10Mar2014
PGH-I-042-7	1. Changed all references from hexane to n-hexane. 2. Added Attachment 2: Horizon Method Summary. 3. General editing for grammar and spelling. 4. Document Reformatted. 5. Update spread sheet as Attachment No 1	13Jun2014
PGH-I-042-8	1. Added to Section 10.4: Stearic acid has a shelf life or five years. Hexadecane has a two year shelf life. 2. Eliminated Section 5.5 due to redundancy.	30Sep2014

Document Number	Reason for Change	Date
	3. Added to Section 11.2: The balance calibration is verified each day of use. The balance verification must be repeated after the samples have all been weighed back.	

20. Equipment Maintenance

20.1 Replace tubing and valves as needed.

21. Method Modifications

21.1 PASI-PGH uses the Horizon Solid Phase Extraction System to prepare the samples instead of separatory funnel extraction.

Attachment No. 1 - Oil & Grease Bench Sheet (Example)

	Initials	Date
OG-EXT	-	-
ANALYSIS	-	-

PACE ANALYTICAL
OIL AND GREASE / TPH
GRAVIMETRIC

Balance Calibration Check
Balance: Sartorius BA2105

True	Initial	Final	Pass
1g	-	-	No
0.002g	-	-	No

Dessicator Time

First Time In: -
First Time Out: -

Time Started: -

Method Number: -

Speed Vap Temp: -

After Inial Weighing Samples returned to Speed vap for continued evaporation.

Second Time in: -
Second Time Out: -

(•) Solid (mg/Kg) ( ) Aqueous (mg/L)

Det. Limit: 5 mg/L for Waters 100mg/Kg for Solids

If <D.L, Report: <5

( ) **Shake** ( ) **Soxhlet** (•) **Horizon**

QC Rec: #DIV/0! QC Rec: #DIV/0! Worksheet: - Batch#: - HBN#: -

Pan Number	Project Number	Sample ID	Samp.Amt. (mL)	Pan + Sample(g) First Drying	Pan + Sample(g) Second Drying	Pan Tare WT. (g)	Weight of O/G (g)	O&G (mg/L)	Raw Wt. of O/G (mg/L)
1	DI	-	-	-	-	-	0	#DIV/0!	0.0
2	LCS	-	-	-	-	-	0	#DIV/0!	0.0
3	-	-	-	-	-	-	0	#DIV/0!	0.0
4	-	-	-	-	-	-	0	#DIV/0!	0.0
5	-	-	-	-	-	-	0	#DIV/0!	0.0
6	-	-	-	-	-	-	0	#DIV/0!	0.0
7	-	-	-	-	-	-	0	#DIV/0!	0.0
8	-	-	-	-	-	-	0	#DIV/0!	0.0
9	-	-	-	-	-	-	0	#DIV/0!	0.0
10	-	-	-	-	-	-	0	#DIV/0!	0.0
11	-	-	-	-	-	-	0	#DIV/0!	0.0
12	-	-	-	-	-	-	0	#DIV/0!	0.0
13	DI	-	-	-	-	-	0	#DIV/0!	0.0
14	LCS	-	-	-	-	-	0	#DIV/0!	0.0
15	-	-	-	-	-	-	0	#DIV/0!	0.0
16	-	-	-	-	-	-	0	#DIV/0!	0.0
17	-	-	-	-	-	-	0	#DIV/0!	0.0
18	-	-	-	-	-	-	0	#DIV/0!	0.0
19	-	-	-	-	-	-	0	#DIV/0!	0.0
20	-	-	-	-	-	-	0	#DIV/0!	0.0
21	-	-	-	-	-	-	0	#DIV/0!	0.0
22	-	-	-	-	-	-	0	#DIV/0!	0.0
23	-	-	-	-	-	-	0	#DIV/0!	0.0
24	-	-	-	-	-	-	0	#DIV/0!	0.0

LCS True Value
42.1 (mg/L)

SOLID RECOVERY LIMITS
O&G
LCS/MS 85-115%
TPH
LCS/MS 70-130%

AQ. RECOVERY LIMITS
O&G
LCS/MS 78-114%
TPH
LCS/MS 64-132%

"-" indicates no data to fill this cell.

WC0170(20JUL2006)

Attachment No.2: Horizon® Method Summary

Horizon technology

Attachment 2: Method Summary

DISK		Method 20: Pacific Premium	Method 21: Pacific Premium	Method 25: Pacific Premium	Method 20: Pacific Premium	Method 30
SIZE (mm)		Clean Sample 47 mm	Dirty Sample 47 mm	Clean Sample 90 mm	Dirty Sample 90 mm	Purge 47 mm disk
PW Hexane	Dispense	6s	6s	10s	10s	1s
	Saturate	1s	1s	1s	1s	0s
	Soak	30s	30s	1Min	1min	0s
	Drain	30s	30s	1Min	1min	6s
PW Methanol	Dispense	6s	6s	10s	10s	1s
	Saturate	1s	1s	1s	1s	0s
	Soak	30s	30s	1min	1min	0s
	Drain	3s	3s	3s	3s	5s
Air Dry		3 min	5 min	3 min	8 min	0s
Rinse #1 - Hexane	Rinse	4s	4s	8s	8s	Methanol Discard - 3s
	Soak	6s	30s	10s	30s	Methanol Discard - 0s
	Elute	26s	15s	15s	15s	Methanol Discard - 6s
Rinse #2 - Hexane	Rinse	2s	3s	7s	7s	Hexane - 3 s
	Soak	45s	45s	45s	1min	Hexane - 0 s
	Elute	45s	45s	40s	45s	Hexane -45 s
Rinse #3 - Hexane	Rinse	2s	3s	7s	7s	
	Soak	45s	45s	45s	1min	
	Elute	30s	45s	30s	30s	
Rinse #4 - Methanol Discard	Rinse	2s	2s	4s	4s	
	Soak	20s	20s	20s	45s	
	Elute*	1min	1min	1min	1min	
Rinse #5 - Hexane	Rinse	2s	2s	4s	4s	
	Soak	45s	45s	45s	45s	
	Elute	45s	45s	40s	45s	
Rinse #6 - Hexane	Rinse	2s	2s	4s	4s	
	Soak	45s	45s	45s	45s	
	Elute	30s	30s	30s	30s	
Rinse #7 - Hexane	Rinse	2s	2s	4s	4s	
	Soak	45s	45s	45s	45s	
	Elute	30s	30s	30s	30s	
Rinse #8 - Hexane	Rinse	2s	2s	4s	4s	
	Soak	45s	45s	45s	45s	
	Dure	1 min	1 min	1 min	1 min	

* Note: "Methanol Discard" indicates that the rinse is going to waste. Use the Standard Header on the controller screen.

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STANDARD OPERATING PROCEDURE

Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT-HEM) Analysis by Hexane Soxhlet Extraction
Method: 9071B

SOP NUMBER:	PGH-I-052-7
REVIEW:	M. Kruth and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-052-6
REVIEW DATE:	Upon Procedural Change

APPROVALS

Marla L. Kruth	6/13/14
Assistant General Manager	Date
Maureen K. DeRubeis	7/11/14
Senior Quality Manager	Date
B. Hamp	7/11/14
Department Manager/Supervisor	Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

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TABLE OF CONTENTS

1. Purpose

1.1 This SOP documents the procedure to be used for the extraction of Hexane Extractable Material (SGT-HEM) as well as Silica Gel Treated Hexane Extractable Material from solid samples by EPA Method 9071B.

2. Scope and Application

2.1 The reporting limit is 100mg/Kg.

2.2 The procedure applies to solid samples, such as sludge, sediment and soils.

2.3 Solid samples other than those mentioned in section 2.1 may also be extracted by this method, provided they fit into the Soxhlet thimble.

2.4 This procedure is used when relatively polar, heavy petroleum fractions are present, or when the levels of nonvolatile greases challenge the solubility limit of the solvent.

2.5 This procedure is suitable for biological lipids, non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related materials.

2.6 This method is NOT recommended for measurement of low-boiling fractions that volatilize at temperatures below 85ºC.

3. Summary of Method

3.1 A representative portion of waste sample is acidified with HCl and dried with magnesium sulfate or sodium sulfate. Magnesium sulfate monohydrate is used to dry acidified sludges which will combine 75% of its own weight in water to form $MgSO_4 \cdot 7H_2O$. Anhydrous Sodium Sulfate is used to dry soils and sediment samples.

3.2 After the sample is dried, it is placed in a Soxhlet thimble and extracted with n-hexane for 4 hours using a Soxhlet apparatus. After the extraction, the n-hexane is evaporated off and the residue in the flask is weighed and reported as hexane extractable material (HEM or O&G).

3.3 If Silica Gel Treated Hexane Extractable Material (SGT-HEM or TPH) analysis is required, the sample is analyzed for the HEM fraction first, then 90mL of n-hexane is added to the flask along with 5g of Silica Gel. 3g of silica gel will absorb 100 mg of HEM. The sample is placed on a stir plate for 5 minutes, filtered into a pre-weighed flask and evaporated to dryness and weighed to determine the SGT-HEM fraction.

4. Interferences

4.1 The procedure is entirely empirical and duplicate results may be obtained only with strict adherence to all details of the process.

4.2 The rate and time of extraction in the Soxhlet apparatus must be exactly as described due to the varying solubility of the various greases.

4.3 The length of time for drying and cooling of extracted material must be constant.

4.4 A gradual increase in mass may result due to absorption of oxygen: a gradual loss of mass may result due to volatilization.

4.5 All glassware must be cleaned with hot water and detergent. After the glassware is washed and rinsed, it is placed in the oven to dry for at least 1 hour before use.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 HEM: Hexane Extractable Material (Oil & Grease)

6.3 SGT-HEM: Silica Gel Treated Hexane Extractable Material (TPH)

6.4 TPH: Total Petroleum Hydrocarbons

6.5 O&G: Oil and Grease.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

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7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples must be collected in glass containers.

8.2 The sample hold time is 28 days from collection.

8.3 Transfer of the n-hexane should not involve any plastic tubing .

8.4 Any turbidity or suspended solids in the extraction flask should be removed by filtering through grease-free cotton or glass wool.

9. Equipment and Supplies

9.1 Soxhlet extraction apparatus.

9.2 Analytical balance (capable of weighing to 0.0001g).

9.3 Vacuum pump or another vacuum source.

9.4 Extraction thimble, cellulose.

9.5 Glass wool or small glass beads to fill thimble.

9.6 Beaker, 150mL.

9.7 Mortar & pestle.

9.8 Flask, boiling.

9.9 Horizon Speed Vap® II 9000 Solvent Evaporation System.

9.10 Desiccator.

9.11 2mg and 1000mg Class S weights.

9.12 Volumetric flask, 200mL, ClassA, glass.

10. Reagents and Standards

10.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.2 Reagent water - All references to water in this method refer to ASTM Type II reagent water.

10.3 Concentrated Hydrochloric acid (HCl)

10.4 Magnesium sulfate monohydrate: Prepare $MgSO_4 \cdot H_2O$ by spreading a thin layer in a dish and drying in an oven at 150ºC overnight.

10.5 Sodium sulfate, granular, anhydrous (Na_2SO_4); Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

10.6 n-Hexane. Purity of 85%, 99.0% minimum saturated. Boiling Point, 69°C. The solvent should leave no measurable residue on evaporation; distill if necessary.

10.7 Heaxadecane/Stearic Acid. 1:1 spiking solution. Prepare in acetone at a concentration of 2 mg/mL each.

10.8 Weigh 800 ± 2mg of stearic acid and 800±2mg hexadecane into a 200ml volumetric flask and fill to the mark with acetone = 8000mg/L HEM. Store in a glass container with a fluoropolymer-lined cap at room temperature. Shield from light. Note: spiking solution may require warming for complete dissolution of the stearic acid.

10.9 Silica Gel, Anhydrous

11. Calibration

11.1 The calibration of the analytical balance must be verified on each day of use prior to the analysis of samples. The calibration of the analytical balance must be verified with a 2 mg and 1000 mg Class S weight prior to and at the conclusion of the mass determinations of the HEM analysis. Calibration shall be within ± 10% (i.e., ± 0.2 mg) at 2 mg and ± 0.5 % (i.e., ± 5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance. The balance is also checked to make sure that it is clean and level.

11.2

11.2.1 If the calibration verification fails, and can not be brought back into specification, the balance is to be tagged as “out of service” and is not to be used until serviced and/or repaired. Documentation of any such service or repair shall be maintained.

12. Procedure

12.1 Sludge Samples

12.1.1 Weigh 10g ± 0.5g for solid samples. Weigh 5 g ± 0.5g of wet sludge samples into a beaker.

12.1.2 Acidify to a pH 2 with approximately 0.3mL of concentrated HCl.

12.1.3 Add 6.25g of $MgSO_4 \cdot H_2O$ and stir to a smooth paste.

12.1.4 Spread the paste on the inside surface of the beaker to facilitate evaporation. Let the sample stand for about 15-30 minutes or until the sample has solidified.

12.1.5 For sample with large particles or clumps, transfer the sample to a mortar and grind to a fine powder.

12.1.6 Transfer the sample to a Soxhlet thimble.

12.1.7 Wipe the beaker and mortar with filter paper moistened with n-hexane and add them to the sample thimble.

12.1.8 Fill the remainder of the thimble with glass beads.

12.2 Solids/Sediments/Soil Samples

12.2.1 Mix the sample thoroughly, discarding any foreign objects such as sticks, leaves and rocks.

12.2.2 Blend 10g sample with 10g sodium sulfate.

12.2.3 Transfer the sample to a Soxhlet thimble.

12.2.4 Fill the remainder of the thimble with glass beads.

12.2.5 The extraction thimble must drain freely for the duration of the extraction period.

12.3 Method Blank, LCS and Spike Samples

12.3.1 Add approximately 20g of glass boiling beads to a thimble. Extract and analyze with the sample batch

12.3.2 Laboratory Control Samples (LCS) - Add 20g glass boiling beads to a thimble and spike with the 4mL of 8,000ppm HEM standard. Final concentration = 1600mg/Kg. The true value for the SGT-HEM is ½ of the HEM (800mg/Kg).

12.3.3 Matrix Spike Sample (MS) - Prepare a second aliquot of one of the samples in the batch for a Matrix Spike sample. Spike the second aliquot with 4mL of 8000 ppm HEM std. Final concentration = 1600 mg/Kg. The true value for the SGT-HEM is ½ of the HEM (800mg/Kg).

12.4 Extraction

12.4.1 Place the thimble in the Soxhlet; add boiling chips and 90mL n-Hexane to the solvent flask then extract the sample at a rate of 20 cycles per hour for 4 hours.

12.4.2 After the extraction is complete, allow the Soxhlet apparatus to cool. Rinse the Soxhlet condenser with n-hexane, catching the rinse solution in the boiling flask containing the n-hexane from the extraction.

12.4.3 In a hood, filter sample through 150mm phase separator paper into a 105mm aluminum pan.

12.4.4 Evaporation of the hexane solvent.

12.4.4.1 Turn on the Speed Vap® II 9000 and set the temperature between 35° and 45° C.

12.4.4.2 Label and pre-weigh clean aluminum pans on a calibrated analytical balance and record the initial masses on a bench sheet.

12.4.4.3 Filter the n-hexane extract into the labeled and pre-weighed pans. Be sure to rinse the flask and the sides of the filter paper with n-hexane.

12.4.4.4 Place the pan with the filtered n-hexane extract in the Speed Vap® II 9000. Close the lid on the Speed Vap® and turn the vacuum knob to the ON position. Adjust the vacuum until there is a gentle swirling motion. Allow the solvent to completely evaporate, and then remove the pans from the Speed-Vap®.

12.4.4.5 Place the pans in a desiccator for 30 minutes and using a balance that has been verified, weigh the pans back and record their masses in the bench sheet.

12.4.4.6 Place the pans back in the Speed-Vap briefly, remove and desiccate for 30 minutes. Weigh pans back the second time recording the weight in the bench sheet.

12.4.4.7 Continue the process until there is less than a 5% or (.0005g) difference between the two weightings.

12.5 TPH Procedure

12.5.1 If Silica Get Treated Hexane Extractable Material (SGT-HEM or TPH) analysis is required, the sample is analyzed for the HEM fraction first.

12.5.2 The silica gel capacity must be determined to ensure that the capacity of the silica gel will not be exceeded. It is presumed that 3 g will normally adsorb 100 mg of all absorbable materials. Use a proportionate amount of silica for HEM above 100 mg, up to a maximum of 30g for 1000 mg HEM.

12.5.3 Add 90mL n-hexane to the pan along with 3g Silica Gel. Place the sample on a stir plate for 5minutes, filtered into a pre-weighed pan and evaporated to dryness. Place the pan in a desiccator for 30 minutes and weigh it to determine the SGT-HEM fraction.

12.6 At the conclusion of the final weigh backs, the balance calibration must be re-verified using a single certified reference weight. The results of the verification are to be documented on the laboratory bench sheet.

13. Calculations

13.1 Not Applicable

14. Quality Control

14.1 A minimum of one blank per analytical batch or twenty samples, whichever is more frequent, must be extracted and analyzed to determine if contamination has occurred.

14.2 One laboratory control sample (LCS) per analytical batch or every twenty samples, whichever is more frequent, must be extracted and analyzed.

14.3 One duplicate per analytical batch or every twenty samples, whichever is more frequent, must be extracted and analyzed to evaluate precision.

14.4 One Matrix Spike sample (client sample spiked with a known amount of target) per batch or every twenty samples, whichever is more frequent, must be analyzed to determine accuracy.

14.5 Corrective Actions for Out-Of-Control Data

14.5.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.5.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.5.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are noted in the final report.

14.5.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.5.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.5.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.5.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.5.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 The method blank must not have any positives present above the reporting limit.

15.2 The %RPD for the duplicate sample must be <20% for O&G and <25% for TPH.

$$\%RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

Where

R1 = Result Sample 1
R2 = Result Sample 2

15.3 The percent recovery for the LCS and MS samples must be ±15% of the true value for O&G and 70-130% for TPH.

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

15.4 If the balance calibration verification performed at the conclusion of the weigh backs is not within the established acceptance criteria, the analyst shall initiate a corrective action to determine the cause of the problem.

15.4.1 Appropriate steps shall be taken to correct the problem and to demonstrate that the balance is back within acceptable limits.

15.4.1.1 All of the samples will be re-weighed, and bracketed with a verification using a certified weight at the end.

15.4.1.2 If the cause can not be determined, the balance will be taken out of service and the samples will be re-weighed on another calibrated balance.

15.4.1.3 The balance will not be returned to service until the cause of the problem is determined and verified to be back within the acceptable limits using certified weights.

15.4.1.4 All records of service and maintenance shall be documented in the balance logbook

15.4.1.5 Corrective actions will be documented in Lab Track.

15.5 Any data that are considered out-of-control will be appropriately flagged as such and qualified in the final report.

15.6 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.7 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.8 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

17. References

17.1 USEPA, SW-846, Method 9071B, *Oil and Grease Extraction for Sludge and Sediment Samples,* III. Ed, Revision 2, April 1998.

17.2 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.3 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.4 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Oil & Grease (gravimetric) bench sheet.

19. Modifications

19.1 The silica gel treatment of the HEM fraction has been added to this SOP to provide a procedure for the analysis of samples for the TPH fraction. This procedure is based on the steps as outlined in EPA 1664A.

19.2 This SOP has been written to use the terms Hexane Extractable Material to refer to Oil & Grease and Silica Gel Treated Hexane Extractable Material to refer to Total Petroleum Hydrocarbon. These terms may be used interchangeably.

19.3 For sludge samples with high water content, a reduced mass of 5g is used.

19.4 Sample are dried using a Speed Vap instead of distillation.

20. Revisions

Document Number	Reason for Change	Date
PGH-I-052-5	1. SOP Review. Updated Cover Page, Headers, Footers to the revision number of this document. 2. Added updateable Table of Contents. 3. All references to Roto-vap concentration and use of flasks have been updated to Speed-Vap® and pans. (Section 12) 4. Added TNI Reference. (Section 17)	29May2012

Document Number	Reason for Change	Date
	5. Fixed Document reference in Revisions table. (Rev 4)	
PGH-I-052-6	1. Hold time added to Section 8.2. 2. Reporting limit added to Section 2. 3. Class S weights added to Section 9. 4. Calibration requirements added to Section 11. 5. Sample weights modified in Section 1.2 6. Filtering process added to Section 12.4.3. 7. Silica gel requirements added to Section 12.5.2. 8. Modification to sludge samples added to Section 19. 9. Speed Vap use added to Section 19. 10. Updated references.	11Mar2014
PGH-I-052-7	1. Eliminated blank correction calculation. 2. General editing for grammar and spelling. 3. Document Reformatted. 4. Update spread sheet as Attachment No. 1	13Jun2014

Attachment No. 1 - Oil & Grease -Gravimetric Bench Sheet (Example)

	Initials	Date
OG-EXT	-	-
ANALYSIS	-	-

PACE ANALYTICAL
OIL AND GREASE / TPH
GRAVIMETRIC

Dessicator Time
First Time In -
First Time Out -
After Inial Weighing Samples returned to Speed vap for continued evaporation.
Second Time in -
Second Time Out -

Balance Calibration Check
Balance: Sartorius BA2105

True	Initial	Final	Pass
1g	-	-	No
0.002g	-	-	No

Time Started: -
Method Number: -
Speed Vap Temp: -

○ Solid (mg/Kg) ◉ Aqueous (mg/L)

Det. Limit: 5 mg/L for Waters 100mg/Kg for Solids

If <D.L, Report: <5

○ **Shake** ○ **Soxhlet** ◉ **Horizon**

QC Rec: #DIV/0! QC Rec: #DIV/0! Worksheet: - Batch#: - HBN#: -

Pan Number	Project Number	Sample ID	Samp.Amt. (ml)	Pan + Sample(g) First Drying	Pan + Sample(g) Second Drying	Pan Tare WT. (g)	Weight of O/G (g)	O&G (mg/L)	Raw Wt. of O/G (mg/L)
1	DI	-	-	-	-	-	0	#DIV/0!	0.0
2	LCS	-	-	-	-	-	0	#DIV/0!	0.0
3		-	-	-	-	-	0	#DIV/0!	0.0
4		-	-	-	-	-	0	#DIV/0!	0.0
5		-	-	-	-	-	0	#DIV/0!	0.0
6		-	-	-	-	-	0	#DIV/0!	0.0
7		-	-	-	-	-	0	#DIV/0!	0.0
8		-	-	-	-	-	0	#DIV/0!	0.0
9		-	-	-	-	-	0	#DIV/0!	0.0
10		-	-	-	-	-	0	#DIV/0!	0.0
11		-	-	-	-	-	0	#DIV/0!	0.0
12		-	-	-	-	-	0	#DIV/0!	0.0
13	DI	-	-	-	-	-	0	#DIV/0!	0.0
14	LCS	-	-	-	-	-	0	#DIV/0!	0.0
15		-	-	-	-	-	0	#DIV/0!	0.0
16		-	-	-	-	-	0	#DIV/0!	0.0
17		-	-	-	-	-	0	#DIV/0!	0.0
18		-	-	-	-	-	0	#DIV/0!	0.0
19		-	-	-	-	-	0	#DIV/0!	0.0
20		-	-	-	-	-	0	#DIV/0!	0.0
21		-	-	-	-	-	0	#DIV/0!	0.0
22		-	-	-	-	-	0	#DIV/0!	0.0
23		-	-	-	-	-	0	#DIV/0!	0.0
24		-	-	-	-	-	0	#DIV/0!	0.0

LCS True Value
42.1 (mg/L)

SOLID RECOVERY LIMITS
O&G
LCS/MS 85-115%
TPH
LCS/MS 70-130%

AQ. RECOVERY LIMITS
O&G
LCS/MS 78-114%
TPH
LCS/MS 64-132%

"-" indicates no data to fill this cell.

WC0170(20JUL2006)

STANDARD OPERATING PROCEDURE

Alkalinity
Method SM 2320B

SOP NUMBER:	PGH-I-015-7
REVIEW:	M. Kruth and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-015-6
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	4/18/13 Date
Senior Quality Manager	7/11/14 Date
Department Manager/Supervisor	7/11/14 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

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Table of Contents

1. Purpose

1.1 This SOP describes the procedure to be used for the analysis of aqueous samples for Alkalinity (Total, Phenolphthalein, Carbonate, Bicarbonate, Hydroxide, free carbon dioxide and total carbon dioxide.)

2. Scope and Application

2.1 This procedure is applicable to drinking, surface and saline waters, domestic and industrial wastes.

2.2 All alkalinity concentration ranges can be determined by this method. These concentration ranges define values for total alkalinity and phenolphthalein alkalinity. Inferences may also be drawn about carbonate, bicarbonate, and hydroxide ion concentrations. However, appropriate aliquots should be used to avoid titration volumes greater than 50mLs. This method is approved for National Pollution Discharge Elimination System (NPDES) testing.

3. Summary of Method

3.1 An unaltered sample (no filtration, dilution, or concentration) is titrated with .02N sulfuric acid to an end-point of pH 8.3 for phenolphthalein alkalinity or pH 4.5 for total alkalinity. If the initial pH of the sample is $\leq$4.5 the alkalinity value is defined as “less than”.

4. Interferences

4.1 When using a pH meter, soaps, oily matter, suspended solids, or precipitates may coat the electrode and can cause sluggish response. Allow additional time between titrant additions with such samples to allow the electrode to reach equilibrium or occasionally clean the electrodes.

4.2 When using a color indicator, samples with turbidity or color can cause problems with the visual identification of the end-point and a pH meter must be used.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2 The alkalinity of water is its acid-neutralizing capacity. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents.

7. Responsibilities and Distribution

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7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples are to be shipped and stored at 4 ± 2^{0}C.

8.2 Avoid sample agitation and prolonged exposure to air.

8.3 Maximum hold time is 14 days from the date of collection.

9. Equipment and Supplies

9.1 Orion 4 Star pH meter and electrode (or equivalent, sensitive to 0.05 pH units)

9.2 Plastic specimen cups (or glass beakers if acidity is also required)

9.3 Magnetic stir plate and stir bars

9.4 25mL Brinkman Digital Burette or equivalent

9.5 50mL volumetric burette graduated to 0.1mL

9.6 50mL, 200mL and 1000mL volumetric flasks

9.7 Analytical balance (Mettler AB204, or equivalent)

9.8 Orion 940/960 pH Meter and Autotitrator, or equivalent

10. Reagents and Standards

10.1 0.05N, Na_2Co_3 (2500/Mg/L) Stock sodium carbonate (Alkalinity) standard: - Weigh 2.5±0.2g sodium carbonate (ACS grade, dried at 250°C for 4 hours and cooled in a desiccator) into a 1L volumetric flask and dilute to the mark with DI water. Record this mass on the bench sheet. Prepare weekly.

10.2 Alkalinity standard (100/Mg/L Na_2CO_3): pipette 8mL of the stock alkalinity standard into a 200mL volumetric flask and dilute to mark with DI water. Prepare weekly or as needed.

10.3 Sulfuric acid: 0.10N and 0.02N (purchased commercially)

10.4 Certified buffer solutions: pH2.00, pH4.00, pH7.00, pH10.00, pH13.00 (purchased commercially from Fisher Scientific, or equivalent).

10.5 Mixed bromcresol green-methyl red indicator solution (pH 4.5 indicator). Dissolve 100mg of bromcresol green sodium salt and 20mg of methyl red sodium salt in 100mL of DI water.

10.6 Phenolphthalein indicator solution (pH 8.3 indicator). May use either the aqueous or alcohol solution:

10.6.1 Aqueous Solution: Dissolve 1g of phenolphthalein disodium salt in a 200mL volumetric flask containing 50mLs of DI water. Dilute to volume with DI water.

10.6.2 Alcohol Solution: Dissolve 1g of phenolphthalein disodium salt in 100mLs of 95% ethyl or isopropyl alcohol and 100mLs of DI water.

11. Calibration

11.1 Manual Titration

11.1.1 Acid Standardization

11.1.1.1 Using a volumetric pipette, add 10mL of the stock alkalinity standard into a 50mL volumetric flask and dilute to the mark.

11.1.1.2 Titrate while stirring the standard with 0.02N acid to a pH of 4.5. Record the volume on the bench sheet. Using the calculations in Section 13, the determined normality is the value used for determining the alkalinity.

11.1.1.3 Pipette 10mL as above and titrate with 0.10N H_2S0_4 to determine the normality used for calculation as above.

11.1.2 pH meter calibration: The measurement system must be calibrated daily with a minimum of three calibration buffer solutions. These solutions must bracket the range of pH values measured. Additional calibration points are recommended provided the pH meter can accept additional calibration data points.

11.1.2.1 Refer to Manual #620 “Orion Star and Star Plus Meter” page number EN-20 and follow the manufacturer’s instructions for calibration of the pH meter.

11.1.2.2 Place aliquots of primary calibration buffers (2.00, 4.00, 7.00, 10.00, 13.00 pH units) into 50mL disposable beakers. Place a stir bar in the beaker, place the beaker on a stir plate, and adjust the stir plate to a moderate speed.

11.1.2.3 Rinse the electrode with DI water and gently wipe with a tissue. Place the pH electrode and ATC electrodes into the primary calibration buffer beaker, taking care to provide adequate clearance for the stir bar but completely immersing the sensing element of the electrode in the solution

11.1.2.4 Follow the manufacturer's instructions for storing the results of each calibration point. Record the results

11.1.2.5 Repeat steps 11.1.2.1 to 11.1.2.4 for the remaining primary calibration buffers.

11.1.2.6 Evaluate the calibration slope. Results for the slope must be within 90-102%. Record the results in the De-Ionized Water Evaluation Logbook specific to the meter being used

11.2 Autotitration using the Orion 940/960

11.2.1 pH Meter Calibration: a calibration is to be analyzed once daily prior to analyzing samples, as required. A three buffer calibration curve (4.00, 7.00, 10.00) is used to bracket the range of measurements being made.

11.2.1.1 Enter Orion pH 940 meter mode. Press SPEED +/- to enter 940 mode from Orion 960 standby mode.

11.2.1.2 Press NO in response to "Operator Menu?"

11.2.1.3 Press YES in response to "Calibrate pH?"

11.2.1.4 Press 3 then YES in response to "Number of Buffers?"

11.2.1.5 Press NO in response to "Do automatic calibration?"

11.2.1.6 Submerge the pH probe, stirrer, and temperature probe in the 4.00 buffer. Press the stirrer button on the titrator control column to begin stirring.

11.2.1.7 Press YES in response to "Electrode placed in buffer 1?"

11.2.1.8 Wait for the probe to stabilize. The Orion 940 will report the measured pH. Record the reported pH in the 940/960 calibration logbook. After stabilization, press YES in response to "Cal as 4.00?"

11.2.1.9 Press the stirrer button on the titrator control column to stop the stirrer. Remove the probes and stirrer from the buffer and rinse.

11.2.1.10 Repeat steps 11.2.1.6 through 11.2.1.9 with the 7.00 and 10.00 buffers.

11.2.1.11 Following calibration, record the reported slope in the calibration logbook the % slope of the calibration curve must be within 90-102%.

11.2.1.12 Press SPEED +/- in response to “Measure pH?” to return to 960 mode.

11.2.1.13 Press YES in response to “Analyze?”

11.2.1.14 Press NO in response to “Model 960 Accessories?”. The 960 is now in standby mode.

12. Procedure

12.1 Sample Preparation

12.1.1 Aqueous - Do not shake, filter, dilute or alter the sample in any way.

12.1.2 Waste – Prepare a water soluble extraction (shake equal amounts by weight of sample and de-ionized water for 20 minutes and filter off the waste. Analyze the aqueous portion).

12.1.3 ASTM leachates may also be analyzed using this procedure.

12.2 Analysis

12.2.1 Manual Titration

12.2.1.1 Pour 50mL of sample into a specimen cup.

12.2.1.2 While maintaining continuous stirring, record the pH of the sample using the calibrated pH meter.

12.2.1.3 Titrate the sample with the 0.02N H_2SO_4 to a pH 8.3 (phenolphthalein) or 4.5 (total) and record the volume of titrant used (in mL) on the benchsheet.

12.2.1.3.1 End point determinations can be determined with a pH meter or with a color indicator that has a well defined end point at the pH being determined.

12.2.1.3.1.1 Any samples with turbidity or that exhibits color must be analyzed on a pH meter. End points determined by color indicator can be verified by pH meter.

12.2.1.3.2 If more than 100mL of titrant is required, start the procedure over with a fresh aliquot of sample and titrate with the 0.10N H_2SO_4.

12.2.1.3.3 A different bench sheet must be used for these high range alkalinity samples, but these samples can be part of the same batch as lower range samples.

12.2.1.3.4 Low Level Alkalinity Determination: (Concentrations <20mg/L). Titrate as above to a pH between 4.3-4.7. Record the volume and exact pH. Carefully add additional titrant until the pH has dropped exactly 0.30pH units. Record the volume of additional titrant used.

12.2.1.4 Transfer the data from the benchsheet to the alkalinity spreadsheet to calculate results.

12.2.1.5 When citing SM2320B as the reference method for the potentiometric titration, the pH of the endpoint used is reported as follows: “The Alkalinity to pH_____=_____mg

$CaCO_3$/L." and indicate clearly if this pH corresponds to an inflection point on the curve.

12.2.2 Orion 940/960 Autotitration

12.2.2.1 Ensure that all necessary probes are seated properly in the 960 autosampler arm. Ensure that the proper titrant with the desired normality is connected to the autodispenser system.

12.2.2.2 Place an empty cup below the titrant dispenser probe, and flush the dispenser system of any old titrant and air bubbles which may negatively affect performance. Press SPEED 5, then YES from 960 standby mode to perform an automatic dispense/flush. Change the dispense quantity to 30 mL to completely flush the entire line. Remove the cup after system flush is complete.

12.2.2.3 Load four rinse cups into the first four positions of the 960 autosampler. The first rinse cup should contain 7.00 buffer solution, while the three remaining cups should contain DI water. Each cup should be filled approximately ¾ full.

12.2.2.4 Load two calibration cups into the next two positions of the 960 autosampler. The first calibration cup should contain 50mL of 4.00 buffer solution and the second calibration cup should contain 50mL of 10.00 buffer solution.

12.2.2.5 Load each of the remaining positions of the 960 autosampler with 50mL of sample as needed.

12.2.2.6 Once the autosampler rack is loaded, Press SPEED 9 from 960 standby mode to enter autosampler mode.

12.2.2.7 Press 2 for the 24-28 cup rack type.

12.2.2.8 Press YES in response to "Autosampler Ready?"

12.2.2.9 Press YES in response to "Calibrate Electrode?"

12.2.2.10 Press 1 to select channel 1 (pH Probe).

12.2.2.11 Press 2 to select Sequences.

12.2.2.12 Set the number of washes to 4 beakers, then press YES.

12.2.2.13 Set the length of each was to 15 seconds, then press YES.

12.2.2.14 Press NO in response to "Keep electrode in Beaker after analysis?"

12.2.2.15 Change the number of samples to reflect the correct number to be analyzed, including all Blanks and QC samples, then press YES.

12.2.2.16 Change the schedule to reflect the desired Alkalinity method to be run, then press YES. A list of current schedules and method specifications can be found in the 940/960 maintenance logbook.

12.2.2.17 If desired, change the sample ID, then press YES.

12.2.2.18 Repeat steps 12.2.2.16 and 12.2.2.17 for each sample.

12.2.2.19 When prompted to "Start Analysis?", ensure that the autotitrator output capture program is running and is connected, then press YES to begin the analysis.

12.2.2.20 Following analysis, save all data from the capture program for printing and transfer to the Alkalinity Benchsheet.

12.2.2.21 Samples which exceed the 100mL titrant limit will be notated in the autotitrator output and should be reanalyzed with a schedule designed for a greater titrant normality.

13. Calculations

13.1 Normality of sulfuric acid:

$$N = \frac{A * B}{53.00 * C}$$

Where:
A = grams Na_2CO_3 /L
B = mL Na_2CO_3
C = mL acid used to titrate

13.2 Total Alkalinity:

$$Alkalinity\ (mg/L\ CaCO_3) = \frac{A * N * 50{,}000}{mL}$$

Where:
A = mL of titrant used to reach total endpoint
N = normality of acid as determined in 13.1
mL = volume of sample

13.3 Low Level Alkalinity (Concentrations <20mg/L)

$$Alkalinity\ (mg/L\ CaCO_3) = \frac{(2B - C) * N * 50{,}000}{mL}$$

Where:
B = mL of titrant used to pH between 4.3 & 4.7
C = mL of titrant used to pH exactly 0.3 units lower
N = normality of acid as determined in 13.1
mL = volume of sample

13.4 Phenolphthalein Alkalinity : $mg/L\ CaCO_3 = \frac{A * N * 50{,}000}{mL}$

Where:
A = mL of titrant used to reach phenolphthalein endpoint
N = normality of acid as determined in 13.1
mL = volume of sample

13.5 Alkalinity relationships – The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters as follows:

13.5.1 Carbonate (CO_3^{-2}) alkalinity is present when phenolphthalein alkalinity≠0 but is less than total alkalinity.

13.5.2 Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

13.5.3 Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity.

13.5.4 The mathematical conversion between hydroxide, carbonate, and bicarbonate alkalinity is shown below where P is the phenolphthalein alkalinity and T is the total alkalinity.

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Alkalinity as $CaCO_3$
P=0	0	0	T
P<1/2T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P=T	T	0	0

13.6 Carbon Dioxide and Forms of Alkalinity by Calculation

13.6.1 Bicarbonate Alkalinity

$$HCO_3^- \_as\_mg\_CaCO_3 / L = \frac{T - 5.0 * 10^{(pH-10)}}{1 - 0.94 * 10^{(pH-10)}}$$

Where:
T= Total alkalinity, mg $CaCO_3$/L

13.6.2 Carbonate Alkalinity

$$CO_3^{-2} as\_mg\_CaCO_3 / L = 0.94 * B * 10^{(pH-10)}$$

Where:
B= Bicarbonate alkalinity, mg $CaCO_3$/L (13.6.1)

13.6.3 Free Carbon Dioxide

$$mg\_CO_2 / L = 2.0 * B * 10^{(6-pH)}$$

Where:
B= Bicarbonate alkalinity, mg $CaCO_3$/L (13.6.1)

13.7 Total carbon dioxide:

$$mg\_total\_CO_2 / L = A + 0.44 * (2B + C)$$

Where:
A = mg free CO_2/L (13.6.3)
B = Bicarbonate alkalinity (13.6.1) and
C = Carbonate alkalinity (13.6.2)

14. Quality Control

14.1 The following controls must be analyzed with each batch of 20 (maximum) samples or daily:

14.1.1 Method Blank – Reagent (DI) water treated exactly the same as a sample – results must be less than the reporting limit.

14.1.2 Laboratory Control Sample – Reagent water with 10mL of the 100mg/L standard added – Percent recovery of the spike must be within ±15% of the true value. TV= 20.0mg/L for Alkalinity and 12.7mg/L for Total CO_2.

14.1.3 Duplicate – A second aliquot of a client sample (other than a field blank) – RPD of the results must be within 20%.

14.1.4 Matrix Spike – A client sample that has been spiked with 2mL of the 2500mg/L standard – Percent recovery of the spikes must be within ±15% of the true value. TV= 100mg/L.

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent (DI) water	One (1) per batch of up to 20 samples. Analyzed at the beginning and end of the batch.	a) Target analytes must be less than reporting limit.	1) Re-analyze associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification. 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS/ICV)	Alkalinity	One (1) per batch of up to 20 samples	% Rec within 85 - 115%	1) Analyze a new LCS. 2) If problem persists, check spike solution. 3) Perform system maintenance prior to new LCS determination. ***Exceptions:*** 1) If LCS %Rec > QC limits and the samples are non-detect, the sample data may be reported with appropriate data qualifiers.

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Matrix Spike (MS)	Alkalinity	One (1) per batch of up to 20 samples	% Rec within 85 - 115%	1) If LCS and MBs are acceptable, the spike results should be reviewed and it may be reported with appropriate footnote indicating matrix interferences.
Duplicate Sample (DUP)	Alkalinity	One (1) per every 20 samples	RPD <= 20%	1) Reanalyze associated samples. *Exceptions:* 1) If sample result is ND, report result without qualification. 2) If sample is just above PRL and duplicate is just below PRL, report without qualifications.

15. Method Performance

15.1 If the result for the Method Blank is greater than reporting limit, evaluate for cause and correct. Re-analyze any batch with a Method Blank that is not acceptable (sample volume permitting).

15.2 If the recovery of the LCS is not acceptable, evaluate for cause and correct. Re-analyze any batch with an LCS that is not acceptable. (sample volume permitting).

15.3 If the RPD for the duplicate is greater than 20%, reanalyze all associated samples and evaluate precision between original and reanalysis.

15.4 If spike acceptance range is not achieved, evaluate the LCS. If it is in control, matrix interference is suspected and must be indicated on the bench sheet and documented in the report. If LCS is not acceptable, reanalyze all associated samples.

15.5 Any data that are considered out-of-control (suspect) or unacceptable will be appropriately flagged and qualified in the analytical report

15.6 Method Performance- is established by the:

15.6.1 Reading and understanding the method and relevant SOP(s).

15.6.2 Analysis of an acceptable initial demonstration of capability (IDOC). Four aliquots of a quality control standard are analyzed.

15.6.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.6.4 Analysis of acceptable semi-annual blind Performance Evaluation samples.

15.6.5 Annual LOD verification.

15.6.6 Analysis of in-house laboratory quality control samples.

15.7 LOD/LOQ

LOQ	10.0 mg/L	MDL	1.68 mg/L

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

16.2 All wastes and samples must be characterized and disposed of in accordance with the PASI waste disposal policy. In general, samples and controls analyzed by this method can be disposed of down the common laboratory drain.

17. References

17.1 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Method 2320B, 1995.

17.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2320B, 1998.

17.3 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500 CO_2-D, 1998.

17.4 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.5 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.6 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No.1 - Alkalinity Bench Sheet

19. Revisions

Document Number	Reason for Change	Date
PGH-I-015-5	1. Annual Review (2011): Updated Cover Sheet, Headers and Footers for this Revision, Added Signature line for Department Supervisor/Manager, Added Annual Review Signature lines (no changes). 2. Section 9: Changed instrument reference (9.1). 3. Section 11: pH meter calibration added (11.1.2). 4. Added Revisions Section (Section 19).	5Apr2011

Document Number	Reason for Change	Date
PGH-I-015-6	1. Added Table of Contents 2. Updated section 11.1.1.2: Using the calculations in Section 13 this determined normality is the value used for determining the alkalinity. 3. Updated section 11.1.2.6: Record the results in the De-Ionized Water Evaluation Logbook specific to the meter being used. 4. Updated section 14.1.4: Percent Recovery of the matrix spike must be within ±15% of the true value. TV=100mg/L. 5. Added Quality Control Table in Section 14. 6. Added Section 15.6: Method Performance is established by… Added sections 15.6.1, 15.6.2, 15.6.3, 15.6.4, 15.6.5. 7. Added Section 15.7 LOD/LOQ. 8. Removed reference to method 310.1. Added TNI Standard reference.	17Apr2013
PGH-I-015-7	1. Added Section 12.2.1.5 2. General Editing for grammar and spelling. 3. Document Reformatted. 4. Updated spread sheet as Attachment No 1	13Jun2014

Attachment No. 1 - Alkalinity Bench Sheet (Example)

ACIDITY/ALKALINITY TEST

PACE ANALYTICAL

Alkalinity Method: 2320 B

Acidity Method: 2310 B(4a)

	Initial:	Date:
TEST BY:	-	-

Worksheet: -
BATCH: -
HBN: -
TIME STARTED: -

Buffer Lot #:	BUFF PH	MET PH	Expir. Date:
WC17-83-1	2	2	1/31/2016
WC18-118-11	4	4	6/30/2016
WC15-143-11	7	7	8/30/2015
WC18-118-9	10	10	3/31/2016
WC16-87-13	13	13	12/31/2014

Meter #:	Orion Star A215
Probe #:	91516
Slope:	-

QC RECOVERY	
True value	20
Obs. Val.:	<10
% Recover	0.00%

Det. Lim.: 10 mg/L
If < MDL report <10 mg/L

SPIKE TRUE VALUE	
Conc.Std.:	1000
ML of Std.	5
MLofSam.:	45
Spk Value:	100

Analytical Spike Recoveries	Spike 1	Spike 2
Spike Val.:	<10	<10
Samp. Val:	<10	<10
% Recov.:	0%	0%
% RPD:	0.00%	

DUPLICATE	Alkalinity	Acidity
Sam. Val.:	<10	<10
Dup. Val.:	<10	<10
% RPD:	0.00%	0.00%

Concentrations	
H2SO4 (N):	0.02
NaOH (N):	0.02

							For Acidity:						
	Proj. #'s:	SAM. ID	SAM. PH	SAM. VOL(mL)	ML PH8.3	ML PH4.5	ML PH4.0	ML pH 8.3	ALK-P mg/L	Alk-T mg/L	CO3-Alk	HCO3-Alk	Acid mg/L	
	DI	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
	LCS	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
1	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
2	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
3	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
4	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
5	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
6	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
7	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
8	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
9	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
10	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
11	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
12	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
13	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
14	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
15	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
16	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
17	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
18	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
19	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	
20	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	Sample ID
DUP	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	-
SPK1	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	-
SPK2	-	-	-	50	-	-	-	-	<10	<10	<10	<10	0	-

"-" indicates no data to fill this cell.

WC001-1(16April2007)

STANDARD OPERATING PROCEDURE

Biochemical Oxygen Demand
And Carbonaceous Biochemical Oxygen Demand
(BOD/CBOD)
Method: SM 5210 B-2001

SOP NUMBER:	PGH-I-009-10
REVIEW:	Tim Harrison and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-009-9
REVIEW DATE:	Upon Procedural Change

APPROVALS

Marla L. Krutti	5/31/14
Assistant General Manager	Date
Maureen K. DeRubeis	7/10/14
Senior Quality Manager	Date
	7/10/14
Department Manager/Supervisor	Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

TABLE OF CONTENTS

SECTION **PAGE**

1. Purpose

   1.1. This SOP documents the procedure to be followed for the analysis of biochemical oxygen demand (BOD) and for carbonaceous biochemical oxygen demand (CBOD) per method SM 5210 B-2001.

2. Scope and Application

   2.1. BOD is an index of the presence of biodegradable substances in a sample. It is fundamentally an empirical parameter. It is applicable to aqueous samples. The abbreviation “BOD-5” refers to a 5 day BOD test.

   2.2. The procedure is also applicable to wastewaters and effluents.

3. Summary of Method

   3.1. The procedure consists of the quantitation of the consumption of molecular oxygen over a five day incubation period. Samples are buffered to an appropriate range of pH. Dilutions of selected quantities of sample are then sealed in airtight bottles together with suitable inorganic buffers and inocula of bacteria selected for their ability to degrade any organic substances present. The bottles are incubated at 20°C and the amount of molecular oxygen consumed in the degradation of the organic components is reported in mg/L.

   3.2. Biochemical oxidation of reduced nitrogen compounds can add a nitrogen demand component to the result. If it is desirable to eliminate this component from the final result, a nitrification inhibitor is added. The result is then exclusively due to carbonaceous pathways and is reported as CBOD (in mg/L).

4. Interferences

   4.1. If nitrification reactions are defined as interference for certain projects, the CBOD result can be provided by this method.

   4.2. The use of clean, well rinsed glassware is particularly important.

   4.3. Lack of an airtight seal or air in the initial bottle preparation can affect results; these are eliminated by the use of correct bottling technique.

   4.4. Photosynthetic reactions produce a positive interference. These are eliminated by incubation in the absence of light.

   4.5. “A number of factors, for example, soluble versus particulate organics, settleable and floatable solids, oxidation of reduced iron and sulfur compounds, or lack of mixing may affect the accuracy and precision of BOD measurements. Presently, there is no way to include adjustments or corrections to account for the effect of these factors.” (Standard Methods, 5210-A,2., page 5-2)

5. Safety

   5.1. Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

   5.2. The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

   5.3. Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1. Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

6.2. Seed: The bacterial inoculum used to decompose the target substances in the sample.

6.3. Polyseed: A well known, EPA approved seed preparation produced by the Inter Bio Corporation, or equivalent.

6.4. Buffer pillow: Commercially prepared plastic ampoules of nutrient buffer used in the preparation of sample dilutions. (Hach Corporation, or equivalent)

6.5. Nitrification inhibitor: A commercially prepared preparation of trichloromethyl pyridine used to produce an oxygen depletion result from carbonaceous degradation only. (Hach Corporation, or equivalent)

6.6. GGA: Glucose-Glutamic Acid, used in aqueous solution in the QC preparations as a nutrient for seed culture; it provides a quantifiable QC analyte. (Labchem, or equivalent)

6.7. Initial DO: The dissolved oxygen value at the start of the incubation period.

6.8. Final DO: The dissolved oxygen value at the end of the incubation period.

6.9. DO Net: The quantity upon which the result is based.

Initial DO - Final DO = DO Net.

7. Responsibilities and Distribution

7.1. General Manager/Assistant General Manager (GM/AGM)

7.1.1. The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2. The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2. Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1. The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2. The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3. The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3. Department Manager/Supervisor

7.3.1. The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2. The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3. The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4. The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4. Individual Staff

7.4.1. Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2. Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3. Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1. Composite Samples: The compositing period should be limited to 24 hours.

8.2. Samples which cannot be analyzed within 2 hours of sampling should be shipped and held at 4±2°C.

8.3. Even at low temperatures, hold time should be kept to a minimum. Samples should be analyzed as soon as possible after sampling, with a maximum hold time of 48 hours.

8.4. Samples are to be unpreserved.

8.5. Chill samples to 20±3°C before analysis.

9. Equipment and Supplies

9.1. Barometer: attached to the LDO probe.

9.2. Electrode Calibration

9.2.1. Large container for dilution water (plastic, ~19L).

9.2.2. Aeration hose and stone.

9.2.3. Siphon hose.

9.2.4. Hach HQ440d Dual-Input, Multi-Parameter Digital Meter with LDO probe(s), or equivalent.

9.2.5. Magnetic stir plate and stir bars.

9.2.6. 300mL Disposable BOD bottles (Fisher Scientific) or equivalent.

9.3. Sample Preparation

9.3.1. pH meter.

9.3.2. Magnetic stir plate and stir bars.

9.3.3. Beakers.

9.3.4. Droppers.

9.3.5. Residual chlorine powder pillows (Hach Corporation, or equivalent).

9.4. Seed Preparation

9.4.1. Analytical balance (Capable of measuring to 0.0001g.)

9.4.2. 1000mL beaker.

9.4.3. Magnetic stir plate and stir bar.

9.4.4. Aeration hose.

9.5. Sample Analysis

9.5.1. 300mL disposable BOD bottles with stoppers and plastic caps (Fisher Scientific), or equivalent.

9.5.2. Disposable pipettes of various size.

9.5.3. Graduated cylinders of various size.

9.5.4. Volumetric pipette, 6mL, Class A

9.5.5. Hach HQ440d Dual-Input, Multi-Parameter Digital Meter with LDO probe(s), or equivalent.

9.5.6. Magnetic stir plate and stir bars.

9.5.7. Air incubator thermostatically controlled at 20±1ºC

10. Reagents and Standards

10.1. Sample Prep Reagents:

10.1.1. 0.1N Sulfuric Acid (H_2SO_4, commercially prepared solution).

10.1.2. 0.1N Sodium Hydroxide (NaOH, commercially prepared solution).

10.2. BOD Analysis Reagents and Standards:

10.2.1. BOD Nutrient buffer pillow (Hach Corporation, or equivalent).

10.2.2. Polyseed Capsules (InterBio or equivalent).

10.2.3. Nitrification inhibitor (Hach Corporation, or equivalent).

10.2.4. Glucose-Glutamic Acid: Use commercially prepared GGA (LabChem Inc, or equivalent). Optionally, if the commercial solution is not available, dissolve 0.15g Glutamic Acid and 0.15g Glucose or Dextrose and dilute to 1000mL in a volumetric flask with distilled water – Prepare daily.

10.2.5. 1:1 Acetic Acid: In a 500mL volumetric flask, add 250mL glacial acetic acid to 250mL DI water. Invert to mix.

10.2.6. 10% Potassium Iodide (KI) solution: In a 100mL volumetric flask add 75mL of DI water and 10g Potassium Iodide. Mix until dissolved and dilute to 100mL with DI water.

10.2.7. Sodium Sulfite (Na_2SO_3) solution: In a 1000mL volumetric flask add 500mL DI water and 1.575g sodium sulfite. Mix until dissolved and dilute to the 1000mL with DI water. Invert to mix. Prepare daily.

10.2.8. Starch Indicator: (Commercially prepared solution, Fisher Scientific, or equivalent).

10.2.9. DPD Chlorine Powder Pillows (Hach Corporation, or equivalent).

11. Calibration

11.1.1. Fill a BOD bottle about ¾ full with DI water (225mL).

11.1.2. Put a stopper in the BOD bottle and shake repeatedly.

11.1.3. Remove the stopper.

11.1.4. Inspect the LDO probe sensor surface. If it is wet, blot it dry with a Kimwipe.

11.1.5. Put the LDO probe in the BOD bottle and allow it to equilibrate. This will take approximately ten minutes.

11.1.6. Select **CALIBRATE,** then **READ**. The display will show **STABILIZING**… and a progress bar as the probe stabilizes in the standard.

11.1.7. The display highlights the standard value. Select **DONE** to view the calibration summary.

11.1.8. Record the barometric pressure from the DO meter.

11.1.9. Select **STORE** to accept the calibration and return to the measurement mode. The calibration record is stored in the probe and the data log.

12. Procedure

12.1. In the following procedure, wherever the instructions are to determine the DO, place the LDO probe into the BOD bottle, start the propeller, press READ, and allow the reading to stabilize on the meter and record the reading on the benchsheet. Be careful not to bend the propeller when inserting or removing the LDO probe.

12.2. Preparation of dilution water

12.2.1. Fill the dilution water container with DI water (~19L).

12.2.2. Aerate for ¼ to ½ hour, using very light bubbling.

12.2.3. Add the contents of 1 Buffer pillow to the aerated water and continue to aerate a few more minutes to mix.

12.3. Preparation of dilution water controls (blanks).

12.3.1. Set up one bottle of aerated unseeded dilution water as a check on the quality of the dilution water by filling one BOD bottle with dilution water.

12.3.2. Determine the initial DO of the water blank. Cap it tightly and incubate.

12.4. Preparation of seed solution.

12.4.1. Add one seed capsule to 550mL of dilution water. Aerate lightly and stir the seed solution for 1 hour before seeding samples. Turn off the stir plate and allow the seed to settle completely (approx. 30 minutes) just before pipetting the seed solution for samples.

12.4.2. Avoid pipetting any solid material to assure uniform seeding of samples.

12.4.3. The manufacturer recommends that the seed solution be used within 6 hours of its preparation.

12.5. Preparation of seed controls.

12.5.1. Set up and label three seed bottles.

12.5.2. Pipette 15mL of seed solution into the 1st bottle.

12.5.3. Pipette 20mL of seed solution into the 2nd bottle.

12.5.4. Pipette 25mL of seed solution into the 3rd bottle.

12.5.5. Finish filling the bottles with unseeded dilution water. Make sure to avoid trapping any air bubbles inside the bottle.

12.5.6. Determine the initial DO, cap tightly and incubate.

12.6. Preparation of the Glucose-Glutamic acid check

12.6.1. Set up 3 bottles for GGA and label accordingly.

12.6.2. Using a class A volumetric pipette, add 6mL of GGA solution to each bottle.

12.6.3. Fill each bottle half full with dilution water.

12.6.4. To each of the three GGA bottles add 4mL of seed solution.

12.6.5. Finish filling the bottles with dilution water. Make sure to avoid trapping any air bubbles inside the bottle.

12.6.6. Determine the initial DO, cap tightly and incubate.

12.7. Seeded BOD 5 day Procedure (BOD5)

12.7.1. Sample temperature should be 20± 3ºC before making dilutions.

12.7.2. Check each sample for the presence of residual chlorine with the Hach DPD chlorine powder pillows. Add 1 pillow to 10mL of sample and swirl sample for 1 minute. Any sign of a red color indicates a positive for chlorine. Document for each sample in the spreadsheet with a "+", indicating positive for chlorine or a "-",indicating a negative for chlorine.

12.7.2.1. If the sample tests positive, add 100mL of neutralized sample to a 250mL beaker. Next, add 1mL 1:1 acetic acid to the sample, followed by a 1mL addition of 10% potassium iodide solution. Gently swirl the sample to mix and add 0.1mL of starch indicator. Note: If the sample does not turn blue add another 0.1mL starch indicator to the sample. Titrate the sample using sodium sulfite until the sample is clear. To the original neutralized sample, add an equivalent amount of sodium sulfite as determined from the above titration. Let the sample stand for 20-30 minutes and recheck the sample for residual chlorine. Record the volume of sodium sulfite that was used on the benchsheet along with sodium sulfite standard identification information.

12.7.2.2. CAUTION: The addition of excess sodium sulfite exerts an oxygen demand and reacts slowly with certain organic chloramine compounds that may be present in chlorinated samples.

12.7.2.3. Check the pH; if it is not between 6.0 and 8.0, adjust the sample temperature to 20±3°C, then adjust the pH to 7.0 -7.2 using a solution of sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) of such strength that the quantity of reagent does not dilute the sample by more than 0.5%. Exceptions may be justified with natural waters when the BOD is to be measured at in-situ pH values. The pH of dilution water should not be affected by the lowest sample dilution. Always seed samples that have been pH adjusted. Name the worksheet (i.e., 1BODmmddyyyy) and upload the sheet. This sheet will be used at the time of BOD reading.

12.7.3. Thoroughly mix the sample then set up a series of three dilutions by adding sample to each of three BOD bottles.

12.7.3.1. Standard dilutions are 10, 30, and 100mL. of sample in each of the three bottles. Additional dilutions should be added for samples of unknown nature.

12.7.3.2. Samples which are visibly high in insoluble matter or which have historical sample data indicating high BOD may require more dilutions or dilutions using less sample.

12.7.3.3. In the absence of prior knowledge, use the following percentages of wastewater when preparing dilutions: 0.01 to 1.0% for strong industrial

wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

12.7.4. Introduce sample directly into the bottle by pipetting the required amount or using a graduated cylinder for larger sample volumes. Allow the sample to flow slowly down the inside edge of the bottle. Avoid any bubbles or unnecessary agitation while pouring.

12.7.5. Add dilution water to fill each bottle half full.

12.7.6. Add 4mL seed solution to each bottle.

12.7.7. Finish filling the bottle with dilution water. Make sure to avoid trapping any air bubbles inside the bottle.

12.7.8. Determine the initial DO of the sample. Open the benchsheet file that was saved earlier. After the sample has stabilized, record the DO level on the benchsheet. Tightly cap the sample, and incubate, at 20±1°C, for 5 days ± 6 hours.

12.7.8.1. Enter <1 for the final D.O. for any dilution that has a result less than 1. Red highlighted cells indicate a numerical value of less than one has been entered and must be corrected for the calculations to work properly in the spreadsheet (e.g., Enter <1).

12.7.9. Rinse the LDO probe with distilled water between sample readings.

12.8. CBOD 5-Day Procedure

12.8.1. Prepare all samples and controls following the BOD procedure as outlined above.

12.8.2. After the addition of the sample, but prior to adding dilution water to each BOD bottle, add the Hach A2533 (TCMP) nitrification inhibitor according to the directions on the dispenser cap. Do not seed the CBOD blank.

12.8.3. Continue analysis as for seeded BOD.

12.9. To cap bottles before incubation, insert the stopper, make a water seal and cover with a plastic cap.

12.10. Incubate all sample bottles and controls for 5 days ± 6 hours at 20 ± 1ºC.

12.11. Recalibrate the LDO meter after 5 days.

12.12. Determine the final DO of all samples. Rinse the LDO probe with distilled water between sample readings.

12.13. Enter all the information from the benchsheet into the BOD spreadsheet for calculations.

13. Calculations

13.1. DO uptake from seed:

$$S = \frac{B_f - B_i}{V_s}$$

S = DO uptake from seed control
B_i = Initial DO of seed control sample
B_f = Final DO of seed control sample
V_s = Volume of seed solution added to seed control

13.2. Average DO uptake from seed added to samples:

$$S_x = \frac{(S_1 + S_2 + S_3) * V_x}{3}$$

Sx = Average DO uptake from seed added to samples
S1 = DO uptake from seed control #1
S2 = DO uptake from seed control #2
S3 = DO uptake from seed control #3
Vx = Volume of seed solution added to sample

Note: Only use the seed controls that have a depleted DO of at least 2mg/L and a final DO of at least 1mg/L.

13.3. Calculating BOD5 (mg/L) for each dilution.

$$BOD5(mg/L) = \frac{((DO_f - DO_i) - S_x) * 300}{P}$$

DOi = initial DO of sample dilution
DOf = final DO of sample dilution
Sx = Average DO uptake from seed added to sample
P = Volume of sample added to BOD bottle.

13.4. Calculating BOD5 (mg/L) for all dilutions that meet criteria

13.4.1. All of the dilutions that have a D.O. depletion of at least 2mg/L and a final D.O. of at least 1mg/L must be included in the final BOD5 average for each sample.

$$Avg\_BOD5(mg/L) = \frac{\sum BOD5(n)}{n}$$

Avg_BOD5= Average BOD5 result in mg/L
BOD5(n) = DO uptake from each dilution that meets criteria (mg/L)
n = number of BOD5 dilutions used for each sample that meet criteria
Note: Only use the seed controls that have a DO depletion of at least 2mg/L and a final DO of at least 1mg/L.

14. Quality Control

14.1. Section 8 suggests some of the problems in evaluating results. It is clear from the literature that Quality Control is a complex problem:

14.1.1. “There is no measurement for establishing bias of the BOD procedure. The glucose-glutamic acid check prescribed is intended to be a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique…”“…many factors affecting BOD tests in multi-laboratory studies (result in) extreme variability in test results…” (Standard Methods, 19th Ed.,p.5-6).

14.2. These observations in the literature reveal the elusive quality of precision and accuracy in this empirical bioassay. The best approach to BOD methodologies (there are many) is to employ carefully standardized materials and equipment and scrupulous technique to control interferences and other variables (See Sections 14,15,19, and 20)

14.3. In addition, three controls are used:

14.3.1. 1 dilution water blank is analyzed per batch.

14.3.2. 3 seed controls are analyzed at 15, 20, and 25mL of seed. This is used to determine the background seed value for calculation. Three dilutions are used in order to ensure a valid background number is obtained.

14.3.3. 3 GGA controls are analyzed; each with 4mL of seed. This is used to demonstrate the suitability of seed and other reagents.

14.4. Corrective Actions for Out-Of-Control Data

14.4.1. Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.4.2. Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.4.3. Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.4.3.1. The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.4.4. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1. Method performance is achieved through reading and understanding the method and the pertinent SOPs, as well as reading and understanding available references such a Standard Methods.

15.2. This procedure requires meticulous technique.

15.3. The glucose-glutamic acid procedure, while not strictly speaking a method control, aids in the evaluation of technique and helps to reveal a breakdown of the method in a given batch.

15.4. Data Assessment and Acceptance Criteria for Quality Control Measures

15.4.1. The initial DO of each sample must be between 7 and 9mg/L. Any reading over 9mg/L (super saturation) may be encountered with cold waters or samples where photosynthesis occurs. To prevent the loss of oxygen during incubation of such samples, reduce the DO to saturation by bringing the sample to 20±3^{o}C in a partially filled bottle while agitating by vigorous shaking. Flag any data in LIMS that has an initial DO reading >9mg/L.

15.4.2. The final DO is required to be at least 1mg/L.

15.4.3. A minimum DO depletion of 2mg/L is required between the initial and final DO.

15.4.4. All dilutions that meet the requirements of final D.O concentration and minimum D.O. depletion shall be used in the final average for the BOD5 result for each sample.

15.4.5. The DO uptake for the blank control must be less than 0.2mg/L. If not, initiate a corrective action to identify the source of the error. Any results reported from a blank control with a DO uptake that is greater than 0.2mg/L must be footnoted in the final report.

15.4.6. The GGA control must fall within the range of 167.5 – 228.5mg/L. Data will be qualified in the final report with a failing GGA.

15.5. Corrective Actions for Out-of Control Data

15.5.1. The best corrective action is re-sampling and reanalysis. Reproducibility of the initial sampling and testing is difficult, but the necessity for minimizing hold time coupled with the five day incubation period precludes other remedies.

15.6. Contingencies for Handling Out-of Control or Unacceptable Data

15.6.1. Any data that are considered out-of-control (suspect) or unacceptable will be appropriately flagged as such and qualified in the analytical report. The final narrative will be determined by one or more of the following parties: the General Chemistry Department Manager/Supervisor, the laboratory's SQM or QM, and/or the GM/AGM..

15.7. Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.8. An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.9. On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1. Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

16.2. All waste generated from this procedure can be disposed of down the common laboratory drains.

17. References

17.1. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.2. TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.3. Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.4. Standard Methods for the Examination of Water and Wastewater, Method 5210-B, 19th Edition, 1995.

17.5. Standard Methods for the Examination of Water and Wastewater Method 5210 B, 20th Edition, 1998.

17.6. Standard Methods for the Examination of Water and Wastewater, Method 5210 B-2001.

17.7. "A Bug's-Eye-View of the BOD Test" Perry Blake, Copyright 2001.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1. Attachment No. 1: BOD Spreadsheet.

19. Method Modifications

19.1. None.

20. Revisions

Document Number	Reason for Change	Date
PGH-I-009-9	1. Added to 11.1.8: Record the barometric pressure from the DO meter. 2. Adjusted Section 12.7.2.3 to updated pH requirements 3. Added Section 12.7.3.3 recommended dilution for unknown samples. 4. Added a note to section 15.4.1 to flag any data that has an initial DO >9 mg/L. 5. Temperature adjustment of samples during prep changed to online method requirement of 20+/-3C in all instances. 6. Added to 15.4.6: Data will be qualified in the final report with a failing GGA.	24Feb2014
PGH-I-009-10	1. Cover and Sections 1.1 and 17.5: revised method reference per latest MUR. 2. General: made editorial corrections. 3. Document Reformatted. 4. Updated spread sheet as Attachment No 1	31May2014

21. Instrument and Equipment Maintenance

21.1. Inspect the LDO probe sensor surface and stir mechanism. Replace when damaged or worn.

Attachment No. 1 - BOD/CBOD Spreadsheet (Example)

Biochemical / Carbonaceous Biochemical Oxygen Demand **Method:** SM 5210 B **Pace Analytical** <2

Analyst:	-	Analyst:	-
Date In:	-	Date Out:	-
Time:	-	Time:	-

page 1 of 2

Average Seed Uptake per ml x 4ml:	0

Seed 1	Seed 2	Seed 3	QC,
15	20	25.00	Seed Volume (ml)
-	-	-	Dissolved Oxygen Initial (mg/l)
-	-	-	Dissolved Oxygen Final (mg/l)
0	0	0.00	Dissolved Oxygen Net (mg/l)
0	0	0.00	Dissolved Oxygen Net (mg/l) per ml of seed

REF QC			Buffer ID#	-	DUPLICATE		Worksheet:	-
	Low	High	Seed ID#	-	Project #/Sample #	-	Batch:	-
Range of QC	167.5	228.5	GGA ID#	-	Original Value:	0.00	HBN:	-
Observed QC 1			Pipette ID#	-	Duplicate Value:	0.00	Start Time:	-
Seed volume added to each sample and QC = 4 ml.			Na2SO3 ID#	-	% RPD	0.00%		
Samples with an initial DO > 9 mg/L must be qualified			Inhibitor ID#	-	**Blank readings > 0.2 mg/L must be qualified.**			

Batch Type: ◉ **BOD** ○ **CBOD**

Initial pH	Final pH	Project Number	Sample Number	Sample Vol. ml	Dilution Factor	Diss. Ox. Initial	Diss. Ox. Final	Diss. Ox. Net	BOD mg/l	Raw Conc. mg/L	Avg BOD Final Value mg/L	Initial Time	Chlorine Check Present (Y/N)	Chlorine Check Titrant Vol (mL)
		BLANK	-	300	1	-	-	0.00	0.00	<2		-	N/A	N/A
		QC-4		6	50	-	-	0.00	0.00	<2			N/A	N/A
		QC-4		6	50	-	-	0.00	0.00	<2				
		QC-4	-	6	50	-	-	0.00	0.00	<2		-		
		-				-	-					-	-	
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				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
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				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
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				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
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				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
-	-	DUP	-	-	#DIV/0!	-	-	0.00	#DIV/0!	0.00		-	-	
				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				
				-	#DIV/0!	-	-	0.00	#DIV/0!	0.00				

Barometric Pressure In	-	0.00
Barometric Pressure Out	-	0.00

COMMENTS :
-

"-" indicates no data to fill this cell. WC003-3 (18DEC2012)

STANDARD OPERATING PROCEDURE

Chemical Oxygen Demand
Method: EPA 410.4

SOP NUMBER:	PGH-I-033-6
REVIEW:	Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-033-5
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	04/22/13 Date
Senior Quality Manager	04/22/13 Date
Department Manager/Supervisor	04/23/13 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

1. Purpose

1.1 This SOP describes the procedure to be used for the analysis of aqueous samples for chemical oxygen demand, by EPA Method 410.4.

2. Scope and Application

2.1 This method applies to the analysis of surface and ground waters and domestic and industrial wastes with low demand characteristics.

2.2 COD is defined as the amount of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. The specified oxidant in this test is the dichromate ion ($Cr_2O_7^{2-}$)

2.3 High level closed reflux tubes are applicable to samples having COD concentrations in the range of 25 to 1500 mg/L. The reporting limit for aqueous samples is 25mg/L.

3. Summary of Method

3.1 Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. Samples are digested at 150°C for 2 hours in sealed vials containing pre-measured amounts of the appropriate reagents. After digestion, the absorbance of the samples is measured at 600nm on a spectrophotometer. Final results are then calculated based on the initial calibration curve.

4. Interferences

4.1 Traces of organic material from the glassware or atmosphere may cause gross, positive error. Extreme care must be exercised to avoid inclusion of organic materials in the deionized (DI) water used for reagent preparation or sample dilution.

4.2 Glassware used in the test should be conditioned by running a blank to eliminate traces of organic material.

4.3 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.4 Chloride is the primary interference, however each COD vial contains mercuric sulfate that will eliminate traces of organic material.

4.5 If a pure green color is obtained in the reacted sample, all the dichromate has been reduced to the chromic state. It will be necessary to repeat the digestion with a diluted sample.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

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7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples should be preserved with sulfuric acid to pH <2 and maintained at 4±2°C until analysis.

8.2 Samples should be collected in glass bottles. It is permissible to use plastic containers if it is known that no organic contaminants are present in the containers.

8.3 Biologically active samples should be tested as soon as possible.

8.4 Samples containing solids should be well mixed, preferably homogenized, to permit removal of a representative aliquot.

8.5 The holding time for COD in 28 days.

9. Equipment and Supplies

9.1 Hach block reactor, capable of maintaining 150°C.

9.2 Hach COD digestion reagent vials: high range (contains the COD reagents $K_2Cr_2O_7$, H_2SO_4 and $HgSO_4$).

9.3 Spectrophotometer, Hach DR 5000, or equivalent.

9.4 Test tube rack.

9.5 Volumetric flasks, 50mL, 100mL, 1L, Class A, glass.

9.6 Volumetric pipettes, assorted volumes as necessary, Class A, glass.

9.7 Electronic balance accurate to 0.0001g.

10. Reagents and Standards

10.1 ASTM Type II (DI) Water (Milli-Q).

10.2 1500mg/L COD Stock solution. Weigh 0.1275g dried (120°C for 2 hours) potassium acid phthalate (KHP) into a 100mL volumetric flask. Dilute to volume with DI water and mix.

10.2.1 Solution is stable when refrigerated and must be replaced every 6 months in the absence of visible biological growth.

10.3 300mg/L COD working solution (LCS/ICV). Measure 10mL of the second source stock solution (See 10.5) into a 50mL volumetric flask. Dilute to volume with DI water and mix well. Prepare fresh daily.

10.4 600 mg/L COD CCV working solution. Measure 20 mL of Primary stock solution into a 50 mL volumetric flask. Dilute to volume with DI water, and mix well. Prepare fresh daily.

10.5 Secondary solutions are to be made of each solution with reagents from a second source (other than that used for the primary solutions) for use as initial calibration confirmation and for spiking.

11. Calibration

11.1 A new calibration curve must be prepared whenever a new stock solution is made or when Quality Control failures indicate the need. The initial calibration is verified by analyzing an ICV (initial control verification) which is a second source standard. Calibration is performed every six months or when the CCV fails. The CCV is analyzed to verify calibration at the beginning of analysis and every 10 samples. The CCV must be same source as calibration standards (primary source standard). The CCV recovery must be within ± 10% of the true value.

11.2 Prepare the following standards by pipetting the following aliquots of the stock solution into 50mL volumetric flasks and diluting to volume with DI water, mix well.

Volume of Stock Solution (mL)	Stock Conc. (mg/L)	Final Volume (mL)	Final Standard Conc. (mg/L)
0.4	750	30	10
1	750	30	25
2	1500	50	60
10	1500	50	300
20	1500	50	600
30	1500	50	900
40	1500	50	1200

11.3 The 25mg/L standard is made by diluting the 1500mg/L stock 1:1 with DI water to create a 750mg/L working solution. 1mL of this working solution is diluted to 30mL with DI water, and mixed well.

11.4 Analyze each of the prepared standards followed by a blank (ICB) as well as an ICV and CCV to verify the calibration. The ICV and CCV recovery must be within ± 10% of the true value.

11.5 Using linear regression, evaluate the points of the curve for linearity. If the correlation coefficient is ≥ 0.995 samples may be analyzed.

12. Procedure

12.1 Preheat the COD reactor to 150°C. Verify the temperature and record the reading in the logbook.

12.2 Sample Preparation:

12.2.1 Pipette 2mL of the sample into a labeled vial. Cap the vial and shake.

12.2.1.1 Use 2mL of DI water for the blank

12.2.1.2 Use 2mL of the working solution for the LCS sample.

12.2.1.3 Spike samples: Mix 9mL of sample with 1mL of the second source solution in a specimen cup. Pipette 2mL of this solution into a vial. If any solution turns green before digestion, the sample needs to be diluted and re-prepared. True Value = 150mg/L.

12.2.2 Set the timer on the digester for two hours. Record the start and end times of the digestion in the logbook.

12.2.3 Heat the vials in the Hach reactor for 2 hours.

12.2.4 At the end of two hours, allow the samples to cool slightly in the reactor. Invert them several times to mix, then allow them to cool to room temperature.

12.3 Turn on the spectrometer and set the absorbance wavelength to 600nm. Allow the instrument to warm up for at least 15 minutes.

12.4 Zero the instrument by placing the blank into the spectrometer and adjusting the zero. The blank must be evaluated at the beginning of each analytical sequence.

12.5 Place each sample tube into the spectrometer and measure its absorbance.

12.5.1 Any sample with an absorbance that exceeds the high standard of the curve must be diluted and reanalyzed.

12.6 Record the absorbance of each sample on the COD bench sheet.

13. Calculations

$$[COD](mg/L) = \frac{(Abs - Intercept)}{Slope} * DF$$

Where:
Abs = Absorbance of Sample after coloring
DF = any dilutions performed

14. Quality Control

14.1 Table 14-1:

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent (DI) water	One (1) per batch of up to 20 samples.	Target analyte must be less than the reporting limit or ½ the reporting limit if required by client.	Reanalyze the method blank once. If still out, re-digest and reanalyze the entire batch if target compound is >RL in the method blank. ***Exceptions:*** 1) If the sample is ND, report sample data without qualification. 2) If the sample result >10x MB detects and the sample cannot be reanalyzed, report sample data with the appropriate qualifier indicating blank contamination.
Laboratory Control Sample (LCS)	COD	One (1) per batch of up to 20 samples,	%Recovery 90 - 110%.	1) Reanalyze the LCS once. 2) If the problem persists, check the spike solution. Reprep and reanalyze the batch with the associated samples if LCS is outside acceptance limits. ***Exceptions:*** If LCS %Recovery is greater than QC limits and the samples are non-detect, the sample data may be reported with appropriate data qualifiers.
Matrix Spike & Matrix Spike Duplicate (MS/MSD)	COD	One MS and one MSD per batch of 10 samples.	%Recovery 90 - 110%. RPD ± 10%.	If LCS and MBs are acceptable, the spike results should be reviewed and it may be reported with appropriate footnote indicating matrix interferences

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	COD	After initial calibration.	%Recovery 90 - 110%.	Reanalyze the ICV once. If it is still outside QC limits, perform system maintenance. Recalibrate the instrument and reanalyze the ICV.
Continuing Calibration Verification (CCV)	COD	Analyzed at the beginning, after every 10 samples, and at end of the batch.	%Recovery 90 - 110%.	If CCV fails, re-analyze the CCV once. If it fails again, reanalyze all affected samples since the last acceptable CCV. If CCV fails again, recalibrate and reanalyze the associated samples since to the last acceptable CCV. Samples must be bracketed with acceptable CCVs.
Initial or Continuing Calibration Blank (ICB/CCB)	Reagent (DI) water	Before beginning a sample run, after every 10 samples, and end of the analysis sequence. ICB/CCB is analyzed after the ICV and CCVs.	Target analyte must be less than the reporting limit or 1/2 the reporting limit if required by client.	Reanalyze the CCB once. If it is still out, correct the problem and re-prep and reanalyze the CCB. All samples following the last acceptable calibration blank must be reanalyzed. Samples must be bracketed by acceptable CCBs.

15. Method Performance

15.1 COD method performance is achieved through the analysis of semi annual MDL verifications, semi annual Performance Evaluation samples and in-house laboratory Quality Control samples.

15.2 Results of for the method blank must be less than reporting limit or less than ½ of the reporting limit if required by client or program.

15.2.1 Evaluate the usability of results for any sample batch where there is a result above the reporting limit. Flag and qualify any data that is used from a batch that has a positive above the reporting limit in the method blank. If the method blank result is greater than the reporting limit, repreparation and reanalysis is required if there are positive results in the samples. If there are recurrent blank results above the reporting limit, corrective action must be taken.

15.3 Recovery for the LCS samples must be within ±10% of the true value.

15.3.1 Evaluate the results of any LCS that has a result that is outside of the acceptance limit. Reanalyze the sample batch if the cause of the unacceptable result cannot be determined.

15.4 Recovery for the CCV samples must be within ± 10% of the true value, 600 mg/L.

15.4.1 The CCV is analyzed every 10 samples. Evaluate the results of any CCV that has a result that is outside of the acceptance limit. Reanalyze the sample batch if the cause of the unacceptable result cannot be determined.

15.5 The RPD for the the MS/MSD or duplicate sample (DUP) must be ≤ 10%.

15.5.1 If the RPD for the (DUP) is greater than 10%, evaluate the results and if no cause for the deviation can be determined, report data with qualification.

15.6 The recovery for the MS and MSD sample must be within ±10% of the true value.

15.6.1 If the percent recovery for the matrix spike (MS) and matrix spike duplicate (MSD) is outside of the acceptance limits, evaluate the results and if no cause for the deviation can be determined, evaluate the LCS. If the spike recovery in the LCS is within the acceptance limit, matrix interference may be assumed and documented in the final report.

15.6.2 The duplicate and matrix spike sample must be varied among the samples provided by the clients. Client supplied field blanks, equipment blanks (rinsates) and trip blanks must not be chosen for the QC samples.

15.6.3 Aqueous LOD/LOQ

LOQ	25 mg/L		
LOD (or MDL)	4.642 mg/L	Effective 10/15/14	LODs are subject to change

15.6.3.1 The LOD (MDL) should be determined every six months.

15.7 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.8 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.9 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

16.2 The vials contain a small amount of hazardous material and any spills must be cleaned up immediately. Cover the contaminated area with sodium bicarbonate or soda ash slaked lime (50:50) and water to make a slurry. Scoop the slurry into a hard plastic chemical resistant container and dispose of it as mercury waste.

17. References

17.1 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.2 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.3 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version

17.4 Hach Method 8000 manual.

17.5 Methods for Chemical Analysis of Water, USEPA 600, Cincinnati, Ohio, Chemical Oxygen Demand USEPA Method 410.4, Rev 2.0. Aug 1993.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No. 1: COD Bench sheet (example)

19. Revisions

Document Number	Reason for Change	Date
PGH-I-033-3	1. SOP Review. Updated Cover Page, Header and Footer information to reflect update. 2. Added updateable Table of Contents. 3. Removed water soluble extraction (Section 12). 4. Added TNI Reference (Section 17). 5. Updated Revision Section (Rev 3).	29May2012
PGH-I-033-4	1. Section 2: Added reporting limit of 25 mg/L. 2. Added Section 11: The initial calibration is verified by analyzing an ICV which is a second source standard. Calibration is performed every six months or when the CCV fails. The CCV is analyzed to verify calibration at the beginning of analysis and every 10 samples. The CCV must be same source as calibration standards (primary source standard). The CCV must be within ± 10%. 3. Added a table for calibration standards in Section 11.2. 4. Added to calibration, ICV must be within ± 10%. 5. Section 14: Replaced current list of QC requirements with QC table. 6. Section 15: Added criteria for method performance and added LOD/LOQ table.	04Mar2012
PGH-I-033-5	1. Edited for spelling and grammar. 2. Changed accuracy of balance to .0001g. 3. The procedure for preparing the 25mg/L standard was corrected (Section 11.3). 4. Document Reformatted. 5. Update spread sheet as Attachment No 1	25Jun2014
PGH-I-033-6	1. Updated table 14-1 overall. Fixed MS/MSD frequency for each batch of 10 samples. Updated the LOD. Added LOD frequency every 6 months. Updated section 15 to be consistent with Table 14-1.	23Apr2015

20. Instrument and equipment maintenance

20.1 HACH DR 5000

20.1.1 Replace the lamp when needed. When the lamp is replaced prepare a new calibration curve. Record all instrument maintenance in the logbook.

20.2 HACH COD reactor digestion block

20.2.1 The thermometer for the digestion block must be calibrated yearly or as needed if temperature drift is noticed.

21. Method Modifications

21.1 The Primary and Secondary Stock solutions are made at a concentration of 1500 mg/L instead of 500 mg/L. (EPA 410.4 rev 2.0, section 7).

21.2 The curve is evaluated to a concentration of 1200mg/L instead of 900mg/L. (EPA 410.4 rev 2.0, section 2).

Attachment No. 1 - COD Bench Sheet (Example)

COD HIGH HACH SPECTROPHOTOMETRIC
410.4 PACE ANALYTICAL

	Initials:	Date:
Test by:	-	-

	REF QC		1	2	3
ml of std.	2	QC VAL. mg/L	300	300	300
conc. Std mg/L	300	Obs. Val. mg/L	-18.72	-18.723575	-18.72
volume mL	2	% REC.	-6.24%	-6.24%	-6.24%

DUPLICATE	
SAM. #:	-
Obs. Val.:	-18.7
Dup. Val.:	-18.7
%RPD	0.00%

Matrix Spike Recoveries and Value			
SAM. #:	-	ml of std	1
Spk 1 val. mg/L	-18.7	conc. Std mg/L	1500
%Rec(1)	-1.25%	vol. sam. mL	9
Spk 2 val. mg/l	-18.7	Spk Val. mg/l	150
%Rec(2)	-1.25%	Samp. Val. mg/L	-18.723575
Spk RPD	0.00%		

Reporting Limit = 25 mg/L MBLK < 1/2 RL
IF <MDL <25 mg/L

	Project Number	Sample ID	Absorb. Measured	Dilution Factor	COD mg/L	Raw Data mg/L
	ICV/LCS 300mg/L	-	-	1	-18.7	-18.7
	CCV 60 mg/L	-	-	1	-18.7	-18.7
	ICB	-	-	1	-18.7	-18.7
1	-	-	-	1	-18.7	-18.7
2	-	-	-	1	-18.7	-18.7
3	-	-	-	1	-18.7	-18.7
4	-	-	-	1	-18.7	-18.7
5	-	-	-	1	-18.7	-18.7
6	-	-	-	1	-18.7	-18.7
7	-	-	-	1	-18.7	-18.7
8	-	-	-	1	-18.7	-18.7
9	-	-	-	1	-18.7	-18.7
10	-	-	-	1	-18.7	-18.7
MBLK	CCB	-	-	1	-18.7	-18.7
ICV/LCS	300 mg/L	-	-	1	-18.7	-18.7
11	-	-	-	1	-18.7	-18.7
12	-	-	-	1	-18.7	-18.7
13	-	-	-	1	-18.7	-18.7
14	-	-	-	1	-18.7	-18.7
15	-	-	-	1	-18.7	-18.7
16	-	-	-	1	-18.7	-18.7
17	-	-	-	1	-18.7	-18.7
18	-	-	-	1	-18.7	-18.7
19	-	-	-	1	-18.7	-18.7
20	-	-	-	1	-18.7	-18.7
DUP	-	-	-	1	-18.7	-18.7
SPK	-	-	-	1	-18.7	-18.7
SPK	-	-	-	1	-18.7	-18.7
	ICV/LCS300 mg/L	-	-	1	-18.7	-18.7
	CCV 60 mg/L	-	-	1	-18.7	-18.7
	CCB	-	-	1	-18.7	-18.7

COD Vial Lot #: -
Worksheet: -
Batch: -
HBN: -
Time Start: -

STD. CURVE DATE
3/17/2014
PREPARED BY:
DLH

Standard mg/L	Absorb.	Std. IDs
10	0.007	-
25	0.015	-
60	0.036	-
300	0.159	-
600	0.284	-
900	0.423	-
1200	0.552	-

Sample ID
-
-
-

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99950755
R Square	0.999015343
Adjusted R	0.998818412
Standard E	0.007424554
Observatio	7

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.279639237	0.279639237	5072.912063	1.03334E-08
Residual	5	0.00027502	5.5124E-05		
Total	6	0.279914857			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.008566472	0.003992685	2.145542022	0.084721287	-0.00169705	0.018829995
X Variable	0.000457523	6.42369E-06	71.22437829	1.03334E-08	0.000441011	0.000474036

Comments: -

"-" indicates no data to fill this cell.

WC005-1 (1 June2010)

STANDARD OPERATING PROCEDURE

Ferrous Iron - Phenanthroline Method
(SmartChem)
Methods: SM 3500-Fe B(20th) / D(19th)

SOP NUMBER:	PGH-I-058-4
REVIEW:	M. Kruth and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-058-3
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	6/13/14 Date
Senior Quality Manager	7/12/14 Date
Department Manager/Supervisor	7/11/14 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

Purpose

1.1. This SOP documents the procedure for the determination of ferrous iron in aqueous samples.

2. Scope and Application

2.1. This procedure is applicable to drinking, surface, and ground waters in the range of 0.1mg/L to 3.0mg/L ferrous iron. The range may be extended by dilution of the samples.

3. Summary of Method

3.1. The 1,10-phenanthroline indicator in the ferrous iron reagent, reacts with any ferrous iron present in the sample to form an orange color. The intensity of the color is proportional to the iron concentration.

3.2. The concentration of ferrous iron is then determined spectrophotometrically by measuring the sample absorbance at 510nm and comparing it to a series of standards.

4. Interferences

4.1. Ferrous iron oxidizes to ferric iron upon exposure to air. Long storage time and exposure to light must be avoided.

4.2. Strong oxidizing agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5mg/L, and nickel in excess of 2mg/L.

4.3. Suspended solids should be removed by filtration.

5. Safety

5.1. Analysts should take necessary safety precautions when handling chemicals and samples.

5.2. Proper personal protection equipment must include, at a minimum, a lab coat, gloves, and safety glasses.

5.3. Analysts should be familiar with the SDS sheets for all chemicals and reagents used in this procedure and the location of the SDS sheets within the laboratory.

5.4. Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

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8. Sample Collection, Preservation, and Handling

8.1. Water samples are collected in plastic bottles and stored at 4 ± 2°C.

8.2. Samples should be analyzed immediately to prevent air oxidation of ferrous iron to ferric iron.

8.3. Sample must be received by the laboratory and analyzed as soon as possible.

8.4. Samples must be warmed to room temperature prior to analysis.

9. Equipment and Supplies

9.1. SmartChem® Discrete Analyzer

9.2. Analytical balance capable of measuring to 0.0001g

9.3. Volumetric pipettes (assorted volumes as necessary), glass, Class A

9.4. 1L, 100mL, and 50mL volumetric flasks, Class A, glass

9.5. Funnels

9.6. 0.45µm membrane filter paper

9.7. SmartChem® software, Version 3.1.14, or equivalent

9.8. Computer compatible to run SmartChem® software.

10. Reagents and Standards

10.1. **Primary Stock Ferrous Ammonium Sulfate Solution (**$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) (100mg/L) – Slowly add 20mL concentrated H_2SO_4 to 50mL DI water in a 1L volumetric flask. Dissolve 0.7022g of ferrous ammonium sulfate, then add 0.1N potassium permanganate drop wise until a faint pink color persists. Dilute to the mark with DI water. 1mL = 100mg/L. This solution is stable for 6 months.

10.2. **Secondary Stock Ferrous Sulfate Solution (100mg/L)** – Slowly add 20 mL of concentrated H_2SO_4 to 50mL of DI water in a 1L volumetric flask. Dissolve 0.4978g of ferrous sulfate then add 0.1 N potassium permanganate drop wise until a faint pink color persists. Dilute to the mark with DI water. 1mL = 100mg/L. This solution is stable for 6 months.

10.3. **Primary Working Standard Solution (10mg/L)** – With a Class A pipette, transfer 10mL Primary Stock ferrous ammonium sulfate solution into a 100mL volumetric flask. Dilute to the mark with DI water. 1mL = 10mg/L. The solution is stable for one month.

10.4. **Secondary Working Standard Solution (10mg/L)** – With a Class A pipette, transfer 10mL Secondary Stock ferrous sulfate solution into a 100mL volumetric flask. Dilute to the mark with DI water. 1mL = 10mg/L. This solution is stable for one month.

10.5. **LCS/ICV (1.0mg/L) –** With a Class A pipette, transfer 5mL Secondary Working Standard Solution into a 50mL volumetric flask. Dilute to the mark with DI water. 1mL = 1mg/L. The solution is stable for one month.

10.6. **CCV (2.0mg/L)** – With a Class A pipette, transfer 10mL Primary Working Standard Solution into a 50mL volumetric flask. Dilute to the mark with DI water. 1mL = 2mg/L. Solution is stable for one month.

10.7. **Matrix Spike** (1.00mg/L) - With a Class A pipette, transfer 10mL of 10 secondary solution in 100mL volumetric flask. Dilute to the mark with sample.

10.8. **Hydroxylamine Hydrochloride** – In a 100mL volumetric flask, add 10g hydroxylamine hydrochloride then dilute to volume with DI water. This solution is stable for 6 months. Concentration = 100g/L.

10.9. **Ammonium Acetate Buffer** – In a 1L volumetric flask, dissolve 250g of ammonium acetate in 150mL DI water. Carefully add 700mL of glacial acetic acid to the volumetric flask then dilute to volume with DI water. The solution is stable for 6 months.

10.10. **Phenanthroline** – In a 100mL volumetric flask, add 100mg Phenanthroline and dilute to volume with DI water. This solution is stable for 6 months.

10.11. Westco rinse solution (surfactant).

11. Calibration

11.1. A new calibration curve and/or standards must be prepared fresh daily, when a new stock is made, when the QC sample fails, or when the instrumentation has changed.

11.2. Prepare a calibration curve by placing 4mL Primary Working Standard Solution into position 1 on the standard tray. Place 5 empty cups in the curve tray. The

SmartChem® will autodilute the 10mg/L standard to produce a curve with the following concentrations: 0.1mg/L, 0.50mg/L, 1mg/L, 2mg/L, and 3mg/L. The calibration curve fit is a linear regression. The coefficient of correlation (r) must be ≥0.995.

11.2.1. Abort the run and recalibrate the instrument if the correlation coefficient is less than 0.995. If the calibration correlation criterion is not met, remake the standards and recalibrate. Instrument maintenance may be required if the problem persists.

11.3. Verify the initial calibration with the analysis of a mid range ICV (1.0mg/L) for each QC batch. The analyzed value must be within ±15% of the true value.

11.4. The primary source CCV (2.0mg/L) will be analyzed at the beginning and the end of each batch. The analyzed value must be within 10% of the true value.

12. Procedure

12.1. Samples that appear to contain a measurable amount of suspended solids must be gravity filtered prior to analysis with a 0.45µm filter.

12.1.1. Fold a 0.45 µm membrane filter and place it into a small glass funnel.

12.1.2. Place the funnel on top of a specimen cup and pour sample into the filter.

12.1.3. Let the sample drain through the filter.

12.1.4. When enough filtrate (>10mL) has collected, discard filter and continue with the analysis.

12.1.5. Place 3mL of sample into a SmartChem® cup and place the cup on the sample tray in the order of the batch worklist.

12.2. Add 0.30mL surfactant to all of the reagents. Mix gently, but do not induce foaming.

12.3. SmartChem® Startup Procedure

12.3.1. Go to Sample Entry.

12.3.2. Double click the Method Run.

12.3.3. Enter the # of samples in the Accept Sample Box.

12.3.4. Click on Accept Samples.

12.3.5. Enter the sample IDs

12.3.6. Review the Run Planner and click Save (red disk in upper right hand corner) that was created.

12.3.7. Go to System Monitor.

12.3.8. Click on the Run Planner.

12.3.9. Verify that this is the correct analytical batch.

12.3.10. Load the samples, standards, reagents, diluent, and empty cups as displayed in the system monitor.

12.3.11. Check the probe rinse, DI water, and Cleaning solution bottles

12.3.12. Click Start.

12.3.13. Click OK to analyze a water baseline (WBL). Cancel to skip the WBL.

12.3.13.1. A WBL should be analyzed a least once a day.

12.3.13.2. The SmartChem® will add 300µL of sample to a cuvette on the reaction tray. It will then add 10µL of hydroxylamine hydrochloride, 30µL acetate

buffer, and 12µL of phenanthroline. The sample read time is 306 seconds at 510nm.

13. Calculations

13.1. Prepare a calibration curve by plotting instrument response against the standard concentrations. Compute sample concentration by comparing the sample response to the standard curve. If necessary, multiply the answer by the appropriate dilution factor. When the SmartChem® is programmed to auto-rerun, dilution corrections will be reported in the results section of the report.

13.2. Calculate the ferrous iron in the original sample as follows:

$$x = \frac{y-b}{m}$$

Where:

y= Absorbance (optimum density)
m= Slope of the of the calibration curve
x= Concentration
b= y- intercept

13.3. Percent Recovery (% Rec) and Relative Percent Differences (RPD) calculations are defined in the Pace Analytical Services, Inc Quality Manual.

14. Quality Control

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One (1) per batch of up to 20 samples	Target analytes must be less than reporting limit.	1) Re-analyze associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification. 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample with qualification to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS/ICV)	Ferrous Iron	One (1) per batch of up to 20 samples	% Rec within 85 - 115%	1) Analyze a new LCS. 2) If problem persists, check spike solution. 3) Perform system maintenance prior to new LCS analysis. ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are ND

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
				in the associated samples, then results may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Ferrous Iron	One (1) per batch of up to 20 samples	% Rec within 85 - 115%	1) If LCS and MBs are acceptable, the spike results should be reviewed and may be reported with appropriate footnote indicating matrix interferences.
Continuing Calibration Verification (CCV)	Ferrous Iron	One (1) per every 10 samples	% Rec within 90-110%	1) If CCV fails re-analyze associated samples.
Duplicate Sample (DUP)	Ferrous Iron	One (1) per batch of up to 20 samples	RPD within ±20%	1) Reanalyze associated samples. *Exceptions:* 1) If sample ND, report sample without. qualification. 2) If sample is just above PRL and duplicate is just below PRL, report without qualifications.

15. Method Performance

15.1. Each analyst must read, understand, and agree to follow this procedure with written documentation maintained in their training file.

15.2. Each analyst must complete an initial demonstration of capability (IDOC) study. Documentation of the IDOC is maintained on file in each analysts training file.

15.3. A method detection limit (MDL) study must be performed annually.

15.4. Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.5. An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.6. On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.7. LOD/LOQ

LOQ	0.1 mg/L		
LOD (or MDL)	0.037mg/L	Effective 6/3/14	LOD is subject to change.

16. Pollution Prevention and Waste Management

16.1. Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

17. References

17.1. Standard Methods for the Examination of Water and Wastewater, 3500-Fe-D., 19th Edition, 1995.

17.2. Standard Methods for the Examination of Water and Wastewater, 3500-Fe-B, 20th Edition, 1998.

17.3. SmartChem® Operations Manual, Westco Scientific Instruments, Inc., Rev 3.0.2

17.4. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.5. TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.6. Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1. Not Applicable.

19. Method Modifications

19.1. The procedure has been adapted from a field method for use on a discrete analyzer.

19.2. Acid addition is being added via the hydroxylamine hydrochloride reagent on the SmartChem®.

19.3. All reagents are being added proportionally to the samples.

19.4. Samples are not being analyzed at the site, but are being analyzed ASAP at the laboratory. Results are flagged appropriately in the laboratory final report.

20. Revisions

Document Number	Reason for Change	Date
PGH-I-058-3	1. Updated Cover page, headers and footers, and table of contents for this revision. 2. Section 10: Primary and Secondary source added to each corresponding stock, working solution and LCS/ICV and CCV. Primary working solution, secondary working solution, CCV, and LCS/ICV are stable for 1 month. 3. 15.4 LOD/LOQ Table added. 4. References to DoD removed. Reference section updated. 5. Added to Section 12.1.5: Place 3mL of sample into a SmartChem® cup and place on sample tray in the order of the batchworklist. 6. Added to section 12.3.13.2: The SmartChem® will add 300®L of sample to a cuvette on the reaction tray. It will then add 10µL of Hydroxylamine hydrochloride, 30µL of Acetate Buffer, and 12µL of Phenanthroline. The sample read time is 306 seconds at 510nm.	17Jan2014

Document Number	Reason for Change	Date
PGH-I-058-4	1. Changed all references from ChemStation® to SmartChem®. 2. General editing for grammar and spelling. 3. Document Reformatted. 4. Added Smartchem Instrument Parameters as Attachment 1 5. Added Smartchem Flag Descriptions as Attachment 2	13Jun2014

21. Instrument and Equipment Maintenance

21.1. Record all maintenance in the maintenance logbook.

21.2. Replace the lamp when there is a noticeable drop in WBL counts or if the bulb is visibly burnt out when the instrument is turned on.

21.3. The cuvettes are to be replaced when there is visible marking on the cuvettes or the WBL keeps failing for a particular cuvette.

21.4. The peristaltic pump tubing should be replaced when the lines are visibly worn, or every three months.

21.5. The drying pad should be replaced when there is visible discoloration on the pad or if the cuvettes fail to pass the WBL..

21.6. The sample needle is replaced when there is noticeable damage to the needle or if the calibration fails after the above actions are performed.

21.7. Refer to the SmartChem® Operations Manual for diagnostics and troubleshooting.

Attachment 1 - SmartChem Instrument Parameters

FE+2 - S-M 3500-FE B Ferrous Iron

Type	: End Point
Direction	: Up
Unit	: mg/L
Model	: Linear
Unit Factor	: 1
Factor	: 1
Decimal	: 4
Slope	: 1
Intercept	: 0
Linearity Low	: 0
Linearity High	: 3
Filter 1	: 510
Fluidics	: No
Sample Blank	: Yes *

RBL 1	: 0.0059
Rbl Replicate	: 3
Use RBL	: Yes
Rgt Rate 1	: 0.0000
E.P. OD Limit	: 0.0015

	Code	Vol	Delay	Read	Rinse
Reagent 1 *	hydr	10	72	0	15
Reagent 2	Buff	30	36	0	15
Reagent 3	Phen	12	0	306	15

Diluent	: DI
Sample Vol	: 300
Dil/Ratio 1	: 1/10
Dil/Ratio 2	: 1/50
Dil/Ratio 3	: 1/100

	Concentration	OD		Concentration	OD
C1	0.1	0	C5	3	0
C2	0.5	0	C6	-	-
C3	1	0	C7	-	-
C4	2	0	C8	-	-

Code	: Fe+2
Description	: Ferrous Iron
Lot#	: 1234
Exp Date	: 12/12/2050
User	: Brayan Hampton
Cal Replicate	: 1
Std - Stock	: 10

Attachment 2 – SmartChem Flags

SmartChem Flag Descriptions

TMP	Temperature Out of Range
SS	Short Sample
SR	Short Reagent
INV	Inversion
EPL	End Point Limit
D	Depletion Limit
FL	First Limit
NL	FIT
R	RBL Out of Range
><	OD Out of Calibration Curve
CV	CV% For Standard Replicates Exceeds Limits
CAL	Calibration Curve Exceeds Limit
L	LOW
H	HIGH
VL	Very LOW
VH	Very HIGH
LA	LOW Alert
HA	HIGH Alert
LL	Linearity LOW
LH	Linearity HIGH
CE	Calculation Error
E	EDIT

STANDARD OPERATING PROCEDURE

Dissolved Oxygen, Membrane Electrode
(SM4500O-G)

SOP NUMBER:	PGH-I-045-5
REVIEW:	M. Kruth and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-045- 4
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	6/13/14 Date
Senior Quality Manager	7/11/14 Date
Department Manager/Supervisor	7/11/14 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

Table of Contents

1. Purpose

1.1 This SOP documents the procedure to be used for the analysis of dissolved oxygen.

2. Scope and Application

2.1 Dissolved oxygen (DO) levels in natural and wastewaters depend on the physical, chemical, and biochemical activities in the body of water. The analysis for DO is a key test in water pollution and waste treatment process control.

2.2 The electrode method for dissolved oxygen is recommended for samples which contain materials such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorate, organic substances readily hydrolized in alkaline solutions, free iodine, intense color or turbidity and biological flocs.

2.3 The electrode method is recommended as a substitute for the modified Winkler procedure for monitoring streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.

2.4 The Practical Quantitation Limit (PQL) for this procedure is 0.1mg/L

3. Summary of Method

3.1 Electrodes for the determination of dissolved oxygen in water are dependant upon electrochemical reactions. The current or potential can be correlated with DO concentrations when analyzed under steady-state conditions. Interfacial dynamics at the electrode/sample interface are a factor in electrode response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

4. Interferences

4.1 Plastic films used with membrane electrodes are permeable to a variety of gases other than oxygen, although no other gas depolarized easily at the indicator electrode. Prolonged use of membrane electrodes in waters containing gases such as hydrogen sulfide tends to lower cell sensitivity. Elimination of this interference is possible through frequently changing and calibrating the membrane electrode.

4.2 Changes in temperature affect both the permeability of the membrane to oxygen and the solubility of oxygen in water. A dual scheme of thermocompensation is incorporated into the electrode. This automatically corrects for both of these effects.

4.3 Dissolved organic materials are not known to interfere in the output from dissolved oxygen electrodes.

4.4 Dissolved inorganic salts are a factor in the performance of dissolved oxygen electrodes.

4.4.1 Electrodes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data. Conversion factors for specific inorganic salts may be developed experimentally. Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

4.5 Reactive compounds can interfere with the output or the performance of dissolved oxygen electrodes.

4.5.1 Reactive gases which pass through the membrane electrodes may interfere. For example, chlorine will depolarize the cathode and cause a high signal output. Long term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the electrode. Alkaline samples in which free chlorine does not exist will not interfere. Hydrogen sulfide will interfere with membrane electrodes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring that all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor to revise SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples should be collected very carefully, avoiding agitation or contact with the air. The collection bottle should be filled completely (no headspace) to avoid air contact.

8.2 Samples must be analyzed as soon as possible after collection.

8.3 Preservation of the sample is not required.

9. Equipment and Supplies

9.1 DO/BOD bottles

9.2 Luminecent Dissolved Oxygen (LDO) electrode with appropriate meter.

10. Reagents and Standards

10.1 Not Applicable

11. Calibration

11.1 Calibration is performed on each day of use prior to sample analysis.

11.2 Fill a DO/BOD bottle with approximately 100mLs of MilliQ water (standard).

11.3 Inspect the LDO electrode sensor surface. If it is wet, blot it dry with a Kimwipe.

11.4 Put the LDO electrode in the DO/BOD bottle and allow approximately ten minutes for it to equilibrate.

11.5 Select “Calibrate” and then “Read”. The display screen will show “Stabilizing…” and a progress bar as the electrode stabilizes in the standard.

11.6 The display highlights the standard value. Select “Done” to view the calibration summary.

11.7 Record the barometric pressure and slope in the comments section of the maintenance logbook.

11.8 Select “Store” to accept the calibration and return to the measurement mode. The calibration is stored in the instrument and the data log.

12. Procedure

12.1 Fill the DO/BOD bottle completely with the sample.

12.1.1 Gently pour the sample down the inside surface of the bottle to avoid agitation or the trapping of air bubbles.

12.2 Insert the electrode into the DO/BOD bottle; be sure that the stirrer on the assembly is stirring gently.

12.3 Be sure the electrode is set on “Measurement mode.”

12.4 Record the reading when the meter stabilizes (approximately one minute). The result displayed is ppm (mg/L) $O_{2,}$ dissolved oxygen.

12.5 Rinse the electrode thoroughly between samples with DI water.

12.6 Place the electrode in a storage bottle when the analysis is complete.

12.6.1 The DO/BOD bottle with approximately 100mLs of MilliQ water in it.

13. Calculations

13.1 Read the dissolved oxygen concentration (in ppm) directly from the meter.

14. Quality Control

14.1 A method blank (DI water) must be analyzed with each sample batch. The results for the method blank must be below the detection limit.

14.1.1 Batches are limited to 20 client samples.

14.2 If enough sample is available, one duplicate sample (DUP) should be analyzed with each sample batch. The Relative Percent Difference (RPD) limit for the duplicate sample is 20%.

14.3 Corrective Actions for Out-Of-Control Data

14.3.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.3.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.3.3 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 Each analyst must read and understand this procedure with written documentation maintained in their training file.

15.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.3 On an annual basis, each analyst will complete a PT sample as a substitute for their continuing demonstration of capability

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials, or spill kits, depending on the amount of and specific substance spilled. Specific protocols

for handling spills are found in the Pace Analytical Chemical Hygiene Plan and in the SDSs.

17. References

17.1 Standard Methods for the Examination of Waters and Wastewaters. 19th Ed., Method 4500-O G., *Dissolved Oxygen Membrane Electrode Method,* 1995.

17.2 Standard Methods for the Examination of Waters and Wastewaters. 20th Ed., Method 4500-O G., *Dissolved Oxygen Membrane Electrode Method,* 1998.

17.3 HACH HQd Laboratory Meter. Basic Users Manual (DOC022.97.80116) 12/2010, Edition 1.

17.4 HACH LBOD101. Basic Users Manual (DOC022.97.80025) 12/2010, Edition 1.

17.5 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.6 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.7 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No. 1: Dissolved Oxygen bench sheet (Example)

19. Revisions

Document Number	Reason for Change	Date
PGH-I-045-3	1. Updated Cover Page, Headers and footers for this revision. 2. Added method reference to the cover page. 3. Changed cover page footer to current PASI copy right footer. 4. Updated Table of Contents to automatically updateable version. 5. (2.4) Added PQL to the SOP. 6. (4.3) Dissolved organic materials are “NOT” known…. 7. (8.1) Clarified that samples are to be shipped without headspace (minimizes changes in DO concentration). 8. (11.1 and 11.2) Changed calibration procedure to manufacturer’s recommendation for the probe. Specified the use of MilliQ water for calibration. 9. (11.8) Recording both barometric pressure and slope in maintenance log (Barometric pressure is for BOD). 10. (12.5) Rinse with DI water. 11. (12.6) Specified storage bottle requirements. 12. (14.1) Defined batch size as 20 samples. MB and DUP made “should” QC samples to match acode requirements. 13. Removed reference to EPA Method 360.1 (17.3). 14. (17.6 & 17.7) Added Manufacturers Manuals for meter and probe as references. (used for source of calibration procedure and troubleshooting. 15. Added Section 20 to SOP.	25Sep2013

Document Number	Reason for Change	Date
PGH-I-045-4	1. Edited for grammar and spelling. 2. Document Reformatted. 3. Update spread sheet as Attachment No 1	13Jun2014

20. Instrument Maintenance, Troubleshooting and Preventative Actions

20.1 See the Troubleshooting Section of the Basic User Manual for the Meter (pgs. 13 and 14)

21. Method Deviations

21.1 None

Attachment No. 1 - Dissolved Oxygen Bench Sheet (Example)

Dissolved Oxygen

Dissolved Oxygen — Pace Analytical

Method: 4500-O G

	Initials	Date			
Analyst:	-	-	-	-	-
			-	-	-

	Project Number	Sample Number	DO mg/L
	DI	-	-
1	-	-	-
2	-	-	-
3	-	-	-
4	-	-	-
5	-	-	-
6	-	-	-
7	-	-	-
8	-	-	-
9	-	-	-
10	-	-	-
11	-	-	-
12	-	-	-
13	-	-	-
14	-	-	-
15	-	-	-
16	-	-	-
17	-	-	-
18	-	-	-
19	-	-	-
20	-	-	-
Dup	-	-	-

Worksheet:	-
Batch:	-
HBN:	-
Start Time:	-

Duplicate	
Sample Number	-
Sample Value	-
Duplicate Value	-
RPD	#VALUE!

Comments: -

-
-
-
-
-
-
-
-

Sample ID
-

"-" indicates no data to fill this cell.

WC009-1(16April2007)

STANDARD OPERATING PROCEDURE

Inorganic Anions by Ion Chromatography
Method: EPA 300.0

SOP NUMBER:	PGH-I-059-7
REVIEW:	Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-059-6
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	06/26/15 Date
Senior Quality Manager	06/26/15 Date
Department Manager/Supervisor	06/26/15 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

SECTION **PAGE**

1. Purpose

1.1 This SOP documents the procedure for the determination of anions (chloride, fluoride, nitrate-N, bromide, nitrite-N, orthophosphate-P, and sulfate) by ion chromatography.

2. Scope and Application

2.1 This is an ion chromatographic (IC) procedure that is applicable to the determination of the above referenced anions in drinking water, surface water and mixed domestic and industrial waste water. See Section 16 for Limits of Detection (LOD). The reporting limits are listed below:

Analyte	**Reporting Limit (mg/L)**
Bromide	0.5
Chloride	0.5
Fluoride	0.1
Sulfate	0.5
Nitrite as N	0.5
Nitrate s N	0.5
Orthophosphate as P	1.0

2.2 This procedure may also be used for the determination of anions in the ASTM extraction of solid samples.

2.2.1 The concentration of anions determined in ASTM extractions of solids by this method measures only those anions that are soluble in the extraction fluid chosen, and may not be representative of the total concentration of the anions present in the solid material.

2.3 This procedure is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method.

3. Summary of Method

3.1 A small volume of sample is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor column, and conductivity detector.

4. Interferences

4.1 Interferences can be caused by substances with retention times that are similar to those of the anions of interest.

4.2 Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

4.3 The water dip, or negative peak, that elutes near the fluoride peak can be eliminated by the addition of the equivalent of 1mL of concentrated eluent to 100mL of each standard and sample.

4.4 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.5 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

5. Safety

5.1 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc – Pittsburgh Quality Manual for the definitions of commonly used laboratory terms used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

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7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

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7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples are to be collected in scrupulously clean glass or polyethylene bottles.

8.2 Sample preservation and holding times for the anions are:

Anion	Preservation	Hold Time
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4ºC	48 hours
Bromide	None required	28 days
Nitrite-N	Cool to 4ºC	48 hours
O-Phosphate-P	Filter & Cool to 4ºC	48 hours
Sulfate	Cool to 4ºC	28 days

8.3 The methods of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment and holding time for the total sample.

9. Equipment and Supplies

9.1 Dionex Ion Chromatograph, DX-500, or equivalent.

9.1.1 Anion guard column, Dionex AG-14, 4mm, (or equivalent.

9.1.2 Anion separator column, Dionex AS-14, 4mm, or equivalent.

9.1.3 Anion self-regenerating suppressor (ASRS), Dionex, or equivalent.

9.1.4 PC with data acquisition and processing software (Peak Net).

9.1.5 AS 40 autosampler, or equivalent.

9.2 Disposable syringe filter, 0.45µm, Gelman, or equivalent.

10. Reagents and Standards

10.1 Distilled water, ASTM type II, conductivity <18µmhos/cm, free of all anions of interest.

10.2 Eluent solution, supplied as a concentrate by Dionex, must be diluted 20 mL to 2.0L with ultra pure DI water. Prepare fresh monthly.

10.3 Calibration and check standards, seven anion mixed, supplied by Dionex. Two separate lot numbers shall be used for calibration and QC analysis.

10.4 CCV: Add 1 mL of the primary source anion standard and dilute to 50 mL of DI water in a 50 ml volumetric. TV= 0.4mg/L for fluoride, 2 mg/L for chloride,

bromide, nitrite, nitrate, sulfate and 4mg/L for phosphate. CCV is good for 48 hours from prep.

10.5 LCS/ICV: Add 1 mL of the second source anion standard and dilute to 50 mL of DI water in a 50 ml volumetric. . TV= 0.4 mg/L for fluoride, 2 mg/L for chloride, bromide, nitrite, nitrate, sulfate and 4 mg/L for phosphate. LCS/ICV is good for 48 hours from prep.

10.6 Matrix Spike: Add 0.2 mL of the second source anion standard to 10mL of sample. TV= 0.4 mg/L for fluoride, 2 mg/L for chloride, bromide, nitrite, nitrate, sulfate and 4 mg/L for phosphate. MS is good for 48 hours from prep.

10.7 **Note:** Standards are purchased in solution. As per manufacturer instructions, these standards are stored in room temperature. .

11. Calibration

11.1 Prepare a minimum of 3 calibration standard dilutions in a range where the majority of samples are expected to fall. Generally 5 calibration standard are used. The calibration is linear where the correlation coefficient (r) must be ≥0.995. A non-linear curve may also be used. If using a non-linear quadratic calibration curve, a minimum of six calibration standards are required. The 2nd order regression will generate a coefficient of determination (COD or r^2) that is a measure of the "goodness of fit" of the quadratic curvature of the data. A value of 1.00 indicates a perfect fit. In order to be used for qualitative purposes, $r^2 \geq 0.990$.

11.2 The initial calibration is verified by analyzing the ICV standard. The continuing calibration is verified every 10 samples by analyzing the CCV standard. The ICV and CCV results must measure ±10% of the true value.

11.3 Calibration Curve (expiration date of 6 months)

Level of Standard	IC Standard Concentration*	Volume of Standard (mL)	Final Volume (mL)	Final Concentration*
Level I	20 /100/ 200	0.25 mL	50	0.1 / 0.5 / 1.0
Level II	20 / 100 / 200	1.25 mL	50	0.5 /2.5 / 5.0
Level III	20 / 100 / 200	2.5 mL	50	1.0 / 5.0 / 10
Level IV	20 / 100 / 200	3.75. mL	50	1.5 /7.5 /15
Level V	20 / 100 / 200	5.0 mL	50	2/ 10 / 20

* Concentration notated as (F^-) / (Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^-) / (PO_4^{-3}) in mg/L

12. Procedure

12.1 Ensure the eluent volume is sufficient to last the duration of the calibration or analytical sequence, and open the nitrogen tank, ensuring a minimum of 90 psi is entering the system line.

12.2 Allow the nitrogen to purge the system for 30 minutes prior to starting the suppressor and pump. Be sure to check that the system is maintaining pressure; otherwise there may be a leak or a cracked fitting. The conductivity reading should be less than 0.1µs/cm prior to the injection of the initial sample.

12.3 Open the shortcut to the MenuDx® icon. In the PeakNet Main Menu, select METHOD EDITOR.

12.4 Select the most recent method to copy. Under data processing, open the fifth box to view and edit the calibration standards.

12.5 Under the tab CALIBRATION STANDARDS, make any applicable changes to the concentrations, always entering the lowest standards first and increasing. This is also the order that the standards are to be entered.

12.6 If it is not practical to use the same number of standards as before, the method will have to be set up from scratch. This is a little more time consuming, and must done from the CONFIGURE tab of the PeakNet® Main Menu.

12.7 Close the METHOD EDITOR, and when prompted, save the method under a new name which is clearly recognizable for future use. Open the RUN command in PeakNet® Main Menu.

12.8 Under FILE, select LOAD METHOD and select the method previously created.

12.9 The method will load, the pump will start, and the suppressor will automatically turn on. The conductivity should lower to near zero prior to commencing any analysis. This may take up to 30 minutes.

12.10 Begin the calibration by selecting the START icon at the top of the screen. Identify the injection as the appropriate calibration standard and be certain to include the calibration standard ID from dilution logbook as part of the name.

12.11 Enter analytical run time in minutes. For all analytes listed, the analytical run time will usually be between 13 and 18 minutes, depending on the pump speed and eluent concentration. If either of these factors cause a 10% change in retention time(s), a new calibration is required.

12.12 Rinse the sample injection syringe at least three times with the standard being analyzed. For injections to be as accurate and consistent as possible, always draw extra fluid into the syringe, invert and point the needle to the ceiling. Tap the syringe until all visible air bubbles have collected at the base of the needle, and expel the fluid until the volume of air free liquid in the syringe is 1.0mL.

12.13 Inject the standard into the injection port and hit START.

12.14 Once the first calibration standard has been analyzed, open the optimize screen in the PeakNet® Main Menu. Open the first calibration standard and ensure that the regions have all been properly identified, and the entire peak is within the highlighted endpoints.

12.15 Shifts endpoints as necessary, being certain to include area to the baseline and omitting area which may falsely be identified as the analyte of interest. See SOP PGH-Q-030 for manual integration procedure.

12.16 When prompted, save the changes to the method. This will update the retention times into the calibration file.

12.17 Proceed with the analysis of the next calibration source, being certain to rinse the injection syringe with that source solution at least 3 times prior to injection.

12.18 Repeat steps 12.12 through 12.17 until all sources have been injected and analyzed.

12.19 Exit the method, by selecting the shutdown method from the file menu. Exit the PeakNet® Run sequence, and enter PEAKNET MODIFY METHOD

12.20 Ensure that the calibration areas match the areas listed in the individual calibration printouts.

12.21 The correlation coefficient (r) must be $\geq$0.995 for all analytes, using either a linear or quadratic equation using the area and ignoring the origin. If using a quadratic calibration curve, a minimum of six calibration standards is required.

12.21.1 Either the low or the high standard may be removed in order to obtain the required correlation coefficient, but a minimum of 3 points must be used for the curve, and all future data will only be reportable between the lowest and highest points used in the curve. If the low standard is dropped and that is at the reporting limit (RL), the RL must be adjusted accordingly. When the highest standard is dropped, more dilutions have to be made when results exceed this level.

12.22 Verify the calibration by performing a CCV using a different source of seven anion standard. All analytes must be within 10% of the known concentration.

12.23 Autosampler Use

12.23.1 On the Dionex Main Screen, select SCHEDULE

12.23.2 Enter sample ID numbers.

12.23.3 Under METHOD, select an Autosampler Method.

12.23.4 Enter data files under current file folder.

12.23.5 Save using the dd/mm/yy format.

12.23.6 Load the autosampler method and turn the gas on.

12.23.7 Allow the baseline to settle. This will take approximately 20 minutes.

12.23.8 Set the autosampler tray up.

12.23.9 Hit the RUN button on the autosampler.

12.23.10 Load the Schedule.

12.23.11 Hit START.

13. Calculations

13.1 Calculate the concentration of the anions in the original sample as follows:

$$x = \frac{y-b}{m}$$

Where:

y= Absorbance (optimum density)
m= Slope of the of the calibration curve
x= Concentration (mg/L)
b= Intercept

14. Quality Control

14.1 Table 1 QC Requirements:

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One (1) per batch of up to 10 samples.	a) Target analytes must be less than reporting limit or ½ the reporting limit if required by client.	Reanalyze the method blank once. If still out, re-digest and reanalyze the entire batch if target compound is >RL in the method blank ***Exceptions:*** 1) If the sample is ND, report the sample without qualification. 2) If the sample result >10x. MB detects and sample cannot be reanalyzed, report the sample with the appropriate qualifier indicating blank contamination.
Laboratory Control Sample (LCS)	Anions	One (1) per batch of up to 10 samples.	% Rec within 90-110%.	1) Reanalyze the LCS once. 2) If the problem persists, check the spike solution. Reprep and reanalyze the batch with the associated samples if LCS is outside acceptance limits ***Exceptions:*** If LCS %Recovery is greater than QC limits and the samples are non-detect, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Anions	One (1) per batch of up to 10 samples.	% Rec within 90-110%.	If LCS and MBs are acceptable, the spike results should be reviewed and may be reported with the appropriate footnote indicating matrix interferences.
Duplicate Sample (DUP)	Anions	One (1) per every 10 samples.	RPD <20%	Reanalyze the sample duplicate. *Exceptions:* 1) If the sample is ND, report the sample result without qualification. 2) If the sample is just above the PRL, and DUP is just below PRL, report the result without qualifications.

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV) [Same source as the LCS]	Anions	After Initial Calibration.	% Rec within 90-110%.	Reanalyze the ICV once. If it is still outside QC limits, perform system maintenance. Recalibrate the instrument and reanalyze the ICV.
Continuing Calibration Verification (CCV)	Anions	Analyzed at the beginning, after every 10 samples, and at end of the batch.	% Rec within 90-110% or If RT is >10% of ICAL RT or the eluent is changed, a new ICAL must be run.	If CCV fails, re-analyze the CCV once. If it fails again, reanalyze all affected samples since the last acceptable CCV. If CCV fails again, recalibrate and reanalyze the associated samples since to the last acceptable CCV. Samples must be bracketed with acceptable CCVs.
Initial or Continuing Calibration Blank (ICB/CCB)	Reagent (DI) water	Before beginning a sample run, after every 10 samples, and end of the analysis sequence. ICB/CCB is analyzed after the ICV and CCVs.	Target analyte must be less than the reporting limit or 1/2 the reporting limit if required by client.	Reanalyze the ICB/CCB once. If it is still out, correct the problem and re-prep and reanalyze the ICB/CCB. All samples following the last acceptable calibration blank must be reanalyzed. Samples must be bracketed by acceptable CCBs.

15. Method Performance

15.1 Method performance is achieved through the analysis of Method Detection Limits (MDLs) or MDL/LOD Verification semi-annually, semi-annual Performance Evaluation samples, DOC performance, and in-house laboratory Quality Control samples. If instrument conditions are changed, a new MDL study should be analyzed.

15.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. LOD/LOQ

Anions	LOQ (mg/L)	LOD/MDL (mg/L)
Fluoride	0.1	0.015
Chloride	0.50	0.09
Bromide	0.50	0.31

Anions	LOQ (mg/L)	LOD/MDL (mg/L)
Nitrite as N	0.50	0.08
Nitrate as N	0.50	0.03
Ortho-phosphate as P	1.0	0.13
Sulfate	0.50	0.07

Note: LODs/MDLs are subject to change, the most recent values are stored in LIMS.

17. Pollution Prevention and Waste Management

17.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

18. References

18.1 U.S. Environmental Protection Agency, "The Determination of Inorganic Anions in Water by Ion Chromatography - Method 300.0", James W. O'Dell, et al, EPA-600/4-84-017 (Mar 1984).

18.2 EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1, August 1993.

18.3 Dionex Corporation DX-500 Operation Manual.

18.4 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

18.5 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

18.6 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18.7 SOP PGH-Q-030, Manual Integration, current version.

19. Tables, Diagrams, Flowcharts, Appendices, etc.

19.1 None.

20. Revisions

Document Number	Reason for Change	Date
PGH-I-059-4	1. Updated the Cover Page, Headers and Footers for this revision. Added Method references to the SOP Title. Copyright footnote on cover page updated to current PASI version. Added Department Supervisor/Manager Signature line to SOP cover page. Updated Table of Contents to the automatic update version. 2. PRLs added for both waters and Leachable anions (Section 16). 3. Direct Injection procedure removed (Section 11). 4. Matrix Spike recoveries changed to 90-110%. 5. Frequency of MDL or MDL verification changed to every 6 months (Section 14.1).	01Oct2013

Document Number	Reason for Change	Date
	6. Section 18: Added the TNI and PASI-PGH QAM references.	
PGH-I-059-5	1. Low level standards and curve removed along with Attachments 1 and 2. 2. Added to Section 11: The calibration is linear where the correlation coefficient (r) must be ≥0.995. The initial calibration is verified by analyzing the ICV standard. The continuing calibration is verified every 10 samples by analyzing the CCV standard. The ICV and CCV criteria are ±10% of the True Value. 3. Added to Section 15.1: If instrument conditions are changed, a new MDL/LOD study should be analyzed. 4. Updated QC Table in section 14: If duplicate sample RPD fails, reanalyze the sample, not the entire batch. 5. Updated references: added current IC method reference.	11Mar2014
PGH-I-059-6	1. Edited for spelling and grammar. 2. Document Reformatted.	25Jun2014
PGH-I-059-7	1. Section 2.1, added RLs. 2. Section 10.4-10.5, updated standard prep and expiration dates. 3. Section 11.1 added calibration criteria for quadratic 4. Section 11.2, updated standard prep for Level 3-5. 5. Section 12.1 added:…analytical sequence… 6. Section 12.15 & 18.7: added reference to manual integration SOP. 7. Section 12.21 added quadratic criteria. Section 12.21.1 added: If the low standard is dropped and that is at the reporting limit (RL), the RL must be adjusted accordingly. When the highest standard is dropped, more dilutions have to be made when results exceed this level. 8. Section 14, updated the QC table 1. 9. Section 10 clarified Nitrite and Nitrate as N and Orhto-phosphate as P. 10. Section 10.7 added storage standard storage requirement. 11. Section 22.1 added: Method 300.0 Section 9.2.2 requires the resulting curve to be linear. Method update Rule May 18, 2012, Federal Register Vol. 77, No. 97, Part II, 40 CFR Parts 136.6 allows use of quadratic curve. MUR describes if the calibration data for a particular analytical method routinely display quadratic character, using quadratic fitting functions may be acceptable. In such cases, the minimum number of calibrators for second order fits should be six, and in no case	25June2015

Document Number	Reason for Change	Date
	should concentrations be extrapolated for instrument responses that exceed that of the most concentrated calibrator. Examples of methods with nonlinear calibration functions include anions by EPA Method 300.0.	

21. Instrument and Equipment Maintenance

21.1 Replace the analytical and guard column as needed. If any of the columns are replaced develop a new calibration.

21.2 Replace Nitrogen as needed.

22. Method Modifications

22.1 Method 300.0 Section 9.2.2 requires the resulting curve to be linear. Method update Rule May 18, 2012, Federal Register Vol. 77, No. 97, Part II, 40 CFR Parts 136.6 allows use of quadratic curve. MUR describes if the calibration data for a particular analytical method routinely display quadratic character, using quadratic fitting functions may be acceptable. In such cases, the minimum number of calibrators for second order fits should be six, and in no case should concentrations be extrapolated for instrument responses that exceed that of the most concentrated calibrator. Examples of methods with nonlinear calibration functions include anions by EPA Method 300.0.

STANDARD OPERATING PROCEDURE

Total Sulfide

SM 4500 S^{2-} F-2000

SOP NUMBER:	PGH-I-010-5
REVIEW:	Tim Harrison and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-010-4
REVIEW DATE:	Upon Procedural Change

APPROVALS

Marla L. Kruth	6/24/14
Assistant General Manager	Date
Maureen K. DeKuiper	7/10/14
Senior Quality Manager	Date
	7/10/14
Department Manager/Supervisor	Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

1. Purpose

1.1. This SOP documents the procedure for the determination of total sulfide in aqueous samples per method SM 4500 S^{2-} F-2000.

2. Scope and Application

2.1. This method is applicable to the measurement of total and dissolved sulfides in surface and saline waters, domestic and industrial wastes.

2.2. Acid insoluble sulfides are not measured by this method.

2.3. This method is only applicable for the measurement of sulfide in concentrations above 1mg/L. The LOQ for sulfide is 1mg/L. The current MDL is available from the quality department.

3. Summary of Method

3.1. Excess iodine is added to a sample which may/may not have been treated with zinc acetate to produce zinc sulfide.

3.2. The iodine oxidizes sulfide to sulfur under acidic conditions.

3.3. The excess iodine is then back-titrated with a sodium thiosulfate solution.

4. Interferences

4.1. Reduced sulfur compounds, such as sulfite, thiosulfate, and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will also give high results.

4.2. Samples must be collected with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an immeasurable form.

4.3. Interferences due to sulfite, thiosulfate, iodide, and other soluble substances (but not ferrocyanide) can be eliminated by first precipitating ZnS, removing the supernatant and replacing it with deionized (DI) water.

5. Safety

5.1. Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.2. The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.3. Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

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6.1. Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

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7.4.3. Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1. Samples are collected in plastic bottles with a minimum of aeration and stored at 4 ± 2°C.

8.2. Samples are preserved to a pH >9 with NaOH and zinc acetate.

8.3. The maximum holding time for preserved samples is 7 days from the time of collection. Unpreserved samples must be analyzed immediately.

9. Equipment and Supplies

9.1. Analytical balance.

9.2. Vacuum system.

9.3. Class A pipettes (assorted volumes as necessary).

9.4. 25mL disposable pipettes.

9.5. 1L and 200mL volumetric flasks, class A, glass.

9.6. Eppendorf pipette and disposable tips, or equivalent.

9.7. Brinkman digital burette (or equivalent).

9.8. 250mL beakers, glass.

9.9. 1000mL filter flask.

9.10. 90mm Buchner funnel.

9.11. 90mm glass fiber filters (0.7 µm).

9.12. 600mL beakers, glass.

9.13. 250mL graduated cylinder.

9.14. 100mL graduated cylinder.

9.15. Stoppered conical flask.

9.16. Aluminum foil.

9.17. Forceps.

9.18. Magnetic stir bars.

9.19. Magnetic stirring plate.

10. Reagents and Standards

10.1. 6N Hydrochloric acid (HCl): To a 1L volumetric flask, add 500mL of DI water and then slowly add 500mL of concentrated HCl.

10.2. Starch Indicator – Fisher Scientific, or equivalent.

10.3. Standard Iodine Solution (0.025N): Weigh and transfer 20-25g potassium iodide (KI) into a 1L volumetric flask using DI water. Add 3.2g of iodine and allow it to dissolve. Dilute the solution to the mark with DI water. Standardize the solution against the sodium thiosulfate solution using a starch indicator as described in Section 11.1. This product can be commercially purchased through Fisher Scientific, or equivalent.

10.4. Standard Sodium Thiosulfate ($Na_2S_2O_3$) Titrant (0.025N): This product is commercially purchased through Fisher Scientific, or equivalent.

10.5. Total Sulfide Standard (570mg/L) – Weigh and transfer 4.07g sodium sulfide (Na_2S) into a 1L volumetric flask with DIwater. Dilute to the mark with DI water. This solution must be made daily. Store in a refrigerator at 4 ± 2°C.

10.6. Total Sulfide LCS/QC Sample (5.70mg/L) - Pipette 2mL of the Total Sulfide Standard into a 200mL volumetric flask and dilute to the mark with DI water. This solution must be made daily.

11. Calibration

11.1. Standardization of Iodine Solution (if made in house):

11.1.1. Measure 5.0mL iodine solution into 100mL DI water.

11.1.2. Add 2mL of 6N HCl and swirl to mix.

11.1.3. Titrate with the sodium thiosulfate titrant to a straw yellow color.

11.1.4. Pipette 2mL starch indicator into the flask. A blue color will appear.

11.1.5. Continue the titration until the blue color disappears.

11.1.6. Record the volume of the total amount of titrant used onto the bench sheet.

12. Procedure

12.1. Unprecipitated sample:

12.1.1. Pipette 5mL of standard iodine solution into a 600mL beaker.

12.1.2. Add DI water to bring volume to approximately 20mL.

12.1.3. Add 2mL of 6N HCl (1:1 HCl) to the solution with an Eppendorf pipette.

12.1.4. Pipette 200mL of sample into the beaker. The pipette tip must be kept below the surface of the iodine solution.

12.1.4.1. For spike samples: pipette 2mL of the sulfide standard into the sample.

12.1.5. If the iodine color disappears after the addition of the sample, add more of the standard iodine solution until the color remains. Record the total volume of the standard iodine solution added in steps 12.1.1 and 12.1.5 on the bench sheet.

12.1.6. Using the digital burette, titrate the contents of the beaker to a straw yellow color with the sodium thiosulfate solution.

12.1.7. Pipette 1mL of starch indicator into the solution. A blue color will appear.

12.1.8. Continue the titration until the blue color disappears.

12.1.9. Record the volume of the total amount of titrant used on the bench sheet.

12.2. Dewatered samples

12.2.1. Set up a 1L filter flask with a Buchner funnel and place a glass fiber filter in the funnel with forceps.

12.2.2. Attach the apparatus to the vacuum system.

12.2.3. Shake the sample vigorously and pour 200mL into a 250mL graduated cylinder.

12.2.4. Pre-wet the filter with DI water and turn on the vacuum.

12.2.5. Slowly pour the sample through the filter. Rinse the graduated cylinder three times with DI water and pour each rinse into the filter.

12.2.6. After all of the liquid has passed through the filter, turn off the vacuum.

12.2.7. Remove the filter from the funnel with the forceps and place it upside down in a 600mL beaker that contains 100mL of DI water.

12.2.8. Pipette 5mL of the iodine solution into the beaker.

12.2.9. Add 2mL of 6N HCl with an Eppendorf pipette.

12.2.9.1. For spike samples: Pipette 2mL of the sulfide standard into the sample.

12.2.10. If the iodine color disappears, add more of the standard iodine solution until the color remains. Record the total volume of the standard iodine solution added in steps 12.2.8 and 12.2.10 on the bench sheet.

12.2.11. Using the digital burette, titrate the contents of the beaker to a straw yellow color with the sodium thiosulfate solution.

12.2.12. Pipette 1mL of the starch indicator into the solution. A blue color will appear.

12.2.13. Continue the titration until the blue color disappears.

12.2.14. Record the volume of the total amount of titrant used on the bench sheet. Results for the dewatered samples are based on the volume of original sample passed through the filter.

13. Calculations

13.1. Calculation for the standardization of Iodine Solution

$$N = A \times B / C$$

Where:

N = Normality of the iodine solution.
A = Normality of the $Na_2S_2O_3$,
B = Volume of $Na_2S_2O_3$ solution used, mL
C = Volume of iodine solution used, mL

13.2. Calculation for the Sulfide content in samples:

$$S=\frac{[(A \times B) – (C \times D)] \times 16{,}000}{E}$$

Where:

S = Sulfide content in the sample, mg/L
A = Volume of iodine solution used, mL
B = Normality of iodine solution,
C = Volume of $Na_2S_2O_3$ solution used (in mL)
D = Normality of $Na_2S_2O_3$ solution,
E = Volume of the sample used, mL

14. Quality Control

14.1. Any data that have to be reported with out-of-control Quality Control items will be qualified appropriately in the final report.

14.2. One method blank (MB) must be analyzed with each batch to demonstrate that the laboratory has not introduced contamination into the samples. The result for the method blank must be below the reporting limit (RL).

14.3. One laboratory control sample (LCS) must be analyzed with each sample batch. The percent recovery for the LCS must be within ±15% of the true value (85-115% recovery). All samples associated with an unacceptable LCS must be reanalyzed.

14.4. One duplicate sample (DUP) must be analyzed with each sample batch. The Duplicate Relative Percent Difference (RPD) acceptance limit is < 20%.

14.5. One spike sample (MS) and matrix spike duplicate (MSD) must be analyzed with each sample batch.

14.5.1. The percent recovery (% R) of the spike sample must be within ± 15% of the true value (85-115% recovery). All samples associated with an unacceptable spike sample must be reanalyzed or reported with appropriate qualification.

14.5.2. If the percent recovery of the spike is outside of the acceptance limits, but the LCS is within range, then matrix interference is suspected.

14.6. Corrective Actions for Out-Of-Control Data

14.6.1. Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.6.2. Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.6.3. Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and the results noted in the final report.

14.6.3.1. An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.6.4. Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.6.5. Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.6.5.1. The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.6.6. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1. Each analyst must read and understand this procedure with written documentation maintained in their training file.

15.2. An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file.

15.3. Periodic performance evaluation (PE) samples are analyzed to demonstrate continuing competence.

15.4. An annual MDL study must be performed.

15.5. Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.6. An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.7. On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1. Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Health and Safety Policy Manual and in the SDSs.

17. References

17.1. Standard Methods for the Examination of Waters and Wastewaters, 19th Ed. Method 4500 S^{2-} F*, Iodometric Method*,1995.

17.2. Standard Methods for the Examination of Waters and Wastewaters, Method 4500 S^{2-} F-2000 and Table 4020:I.

17.3. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.4. TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.5. Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1. Attachment No. 1: Total Sulfide bench sheet.

19. Revisions

Document Number	Reason for Change	Date
PGH-I-010-4	1. Added method number to title. 2. Section 2.3 added RL/LOQ. 3. Section 10 revised, most reagents are now purchased. 4. References to EPA method 376.1 and SW 846 9034 have been removed (Section17).	18Jan2013
PGH-I-010-5	1. Cover and sections 1.1 and 17.3: revised method reference per latest MUR. 2. Section 2.1: removed reference to drinking water matrix (not in method). 3. Section 15.4: added section for MDL study. 4. General: made editorial corrections. 5. Document Reformatted. 6. Updated spread sheet as Attachment No 1	24Jun2014

Attachment No. 1
Sulfide Bench Sheet (Example)

SULFIDE ANALYSIS Pace Analytical

Test.	-	Date	-

Sodium Thiosulfate Standardization
Chem ID #: WC15-33-01
Lot #: 2308715
Exp. Date: January-15
0.025 Average Thiosulfate Standardization (N)

Det. Lim. for Water: 1 mg/L
Det. Lim. for Waste: 10 mg/Kg
If < D.L. for Water, report: <1
If < D.L. for Waste, report: <10

Method:
(•) 4500-S-2 F (mg/L)
( ) 7.3.4.2 (mg/Kg)

Iodine Standardization
Chem ID #: WC15-163-05
Lot #: 2309878
Exp. Date: September-14
0.025 Average Iodine Standardization

LCS Recovery (mg/L)	
True Value:	5.7
Result	0
Rec.	0.00%

	Project Number	Sample Number	Smpl.Vol. g	Iodine Sol. ml	Na2S2O3 Final ml	Na2S2O3 Init. ml	Net ml Na2S2O3	Sulfide (mg/L)	Raw Conc. (mg/L)
	ICB	DI	200	-	-	0	0	0.0000	0.0000
	LCS	-	200	-	-	-	0	0.0000	0.0000
1	-	-	-	-	-	-	0	#DIV/0!	0.0000
2	-	-	-	-	-	-	0	#DIV/0!	0.0000
3	-	-	-	-	-	-	0	#DIV/0!	0.0000
4	-	-	-	-	-	-	0	#DIV/0!	0.0000
5	-	-	-	-	-	-	0	#DIV/0!	0.0000
6	-	-	-	-	-	-	0	#DIV/0!	0.0000
7	-	-	-	-	-	-	0	#DIV/0!	0.0000
8	-	-	-	-	-	-	0	#DIV/0!	0.0000
9	-	-	-	-	-	-	0	#DIV/0!	0.0000
10	-	-	-	-	-	-	0	#DIV/0!	0.0000
11	-	-	-	-	-	-	0	#DIV/0!	0.0000
12	-	-	-	-	-	-	0	#DIV/0!	0.0000
13	-	-	-	-	-	-	0	#DIV/0!	0.0000
14	-	-	-	-	-	-	0	#DIV/0!	0.0000
15	-	-	-	-	-	-	0	#DIV/0!	0.0000
16	-	-	-	-	-	-	0	#DIV/0!	0.0000
17	-	-	-	-	-	-	0	#DIV/0!	0.0000
18	-	-	-	-	-	-	0	#DIV/0!	0.0000
19	-	-	-	-	-	-	0	#DIV/0!	0.0000
20	-	-	-	-	-	-	0	#DIV/0!	0.0000
Dup	-	-	-	-	-	-	0	#DIV/0!	0.0000
MS	-	-	-	-	-	-	0	#DIV/0!	0.0000
MSD	-	-	-	-	-	-	0	#DIV/0!	0.0000

Duplicate Recovery	
Sample	-
Result	#DIV/0!
Dup	#DIV/0!
RPD	0.00%

Spike Recovery (mg/L)	
True Value:	5.7
Sample	-
Result	#DIV/0!
MS	#DIV/0!
Recovery	#DIV/0!
MSD	#DIV/0!
Recovery	#DIV/0!
Spk RPD	0.00%

Sample ID	
Dup	-
MS	-
MSD	-

Worksheet: -
Batch: -
HBN: -
Start Time: -

Observations: -

"-" indicates no data to fill this cell.

WC027-1(16April2006)

STANDARD OPERATING PROCEDURE

Total Organic Carbon

Methods: SM 5310C and EPA 9060/9060A

SOP NUMBER:	PGH-I-060-6
REVIEW:	B. Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-060-5
REVIEW DATE:	Upon Procedural Change

APPROVALS

Penelope J Westrick

Assistant General Manager — 12/31/14 Date

Maureen K. DeRubeis

Senior Quality Manager — 12/19/14 Date

Department Manager/Supervisor — 12/19/14 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

Table of Contents

1. Purpose

1.1 This SOP documents the procedure for the determination of total organic carbon in aqueous samples.

2. Scope and Application

2.1 This procedure is applicable to drinking, surface, and ground waters in the range of 1.0mg/L to 100mg/L of TOC. The range may be extended by dilution of the samples. The reporting limit is 1.0 mg/L.

2.2 The forms of carbon that can be measured include:

2.2.1 Soluble, nonvolatile organic carbon, (i.e., natural sugars)

2.2.2 Soluble, volatile organic carbon, (i.e., Mercaptans, alkanes, low molecular weight alcohols)

2.2.3 Insoluble, partially volatile carbon, (i.e., Low molecular weight oils)

2.2.4 Insoluble, particulate carbonaceous materials, (i.e., cellulose fibers)

2.2.5 Soluble or insoluble carbonaceous materials absorbed or entrapped on insoluble inorganic suspended matter, (i.e., oily matter absorbed on silt particles)

3. Summary of Method

3.1 Total Organic Carbon (TOC) is measured with a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by wet chemical oxidation.

3.2 The sample is first acidified and purged of Total Inorganic Carbon (TIC), then sodium persulfate ($Na_2S_2O_8$), a strong oxidizer, is added at 100°C to quickly react with the organic carbon in the sample at to form CO_2.

3.3 When the oxidation reaction is complete, the CO_2 is purged from the solution, concentrated by trapping, then desorbed and carried into a non-dispersive infrared analyzer (NDIR) which has been calibrated to directly display the mass of CO_2 detected.

3.4 The resulting carbon mass in the form of CO_2 is equivalent to the mass of organic carbon originally in the sample.

4. Interferences

4.1 Major sources of contamination may be attributed to purge/carrier gas, reagent water, reagents, glassware, and other sample processing equipment. Contamination from these sources are detected and/or minimized by the use of ultra high purity gases, the analysis of method blanks, and by the use of properly cleaned glassware.

4.2 The sample matrix may cause additional interferences. For example, pickle liquors are very acidic and may contain substances that produce unreliable or erratic responses. Significant dilutions of samples with these types of matrices may be performed during the initial analysis to minimize the effect and to prevent damage to the TOC analyzer.

4.3 Samples with high concentrations of TOC may be a source of system contamination caused by the “carry over” of organic carbon into following sample analyses. Carry over may be confirmed if the analysis following a highly concentrated sample appears to be equally concentrated. This is especially common after the analysis of samples with concentrations of organic carbon > the instrument calibration range (100mg/L or above). A method blank must be analyzed immediately following the analysis of such samples until a blank value of less than 1.0mg/L carbon is achieved.

5. Safety

5.1 All reagents and samples are to be handled with caution. Fume hoods are available for use when preparing reagents and stock solutions. Refer to Pace Analytical's Chemical Hygiene Plan, and 29CFR Section 1910.1450 – Occupational Exposure to Hazardous Chemicals in Laboratories for further guidance regarding specific laboratory policies.

5.2 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.3 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.4 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples are collected without headspace in amber bottles to prevent light-initiated degradation of analytes within the sample.

8.2 Samples are acidified to pH <2.0 with H_2SO_4 for preservation.

8.3 TOC samples must be shipped and analyzed within 28 days of collection.

8.4 Samples for TOC analysis are stored in a refrigerator at 4±2 °C, away from sunlight and atmospheric oxygen.

8.5 Samples are stored separately from stock standards, working standards, neat materials, reagents, and solvents

8.6 Samples containing large particles must be homogenized.

8.6.1 All samples for EPA Method 9060/9060A should be homogenized in a blender prior to analysis.

9. Equipment and Supplies

9.1 Owens Illinois (OI) Analytical Aurora Model 1030 Total Organic Carbon analyzer (or equivalent).

9.2 OI autosampler model 1088 A/S (or equivalent).

9.3 40mL VOA vials, glass, with caps.

9.4 Nitrogen Gas- Ultra High Purity Grade

9.5 100mL Volumetric flasks, Class A, glass, 50mL, 100mL, and 1L.

9.6 1, 5, and 10mL Class A pipettes

9.7 P-4 filter paper

9.8 Analytical balance capable of measuring 0.0001g

9.9 Computer system capable of acquiring and processing the data from the automated system

9.10 Blender

10. Reagents and Standards

10.1 All reagents and standard solutions are documented in a standard preparation logbook.

10.1.1 Documentation includes a unique ID number, solution type, concentration, manufacturer and expiration date for the stock used, the date prepared, initials of the analyst and an expiration date for the current solution.

10.1.2 Reagent and standard labels include the standard preparation logbook ID number, solution type, concentration, preparation date, analyst's initials, and expiration date.

10.2 Reagents

10.2.1 DI water (ASTM Type II/Milli Q)

10.2.2 Phosphoric Acid Solution (5.0% vol/vol):

10.2.2.1 Add 59.0mL of ACS reagent grade 85.0% H_3PO_4 to a 1L volumetric flask containing 250-500mL reagent water. The solution is mixed and brought to final volume with DI water. The solution may be used for 1 month from preparation.

10.2.3 Sodium Persulfate (20%):

10.2.3.1 Add 200.0g of $Na_2S_2O_8$ to a 1L volumetric flask containing 250-500mL reagent water. The solution is mixed and brought to final volume with DI water. The solution is stored in a labeled, 1L, clear glass bottle. The solution may be used for 1 month from preparation.

10.2.4 Concentrated Sulfuric Acid (H_2SO_4).

10.3 Stock Solutions

10.3.1 Potassium Hydrogen Phthalate (KHP), Primary Stock Solution (1000mg/L C): Add 0.2128g of KHP to a 100mL volumetric flask containing 50mL reagent water. The solution is mixed and brought to final volume with DI water. The solution is refrigerated at 4.0°C. The solution may be used for 6 months from preparation.

10.3.2 Secondary 1000mg/L C stock solution is to be made with a KHP reagent with a different lot number than the primary source. The solution is refrigerated at 4.0° C. The solution may be used for 6 months from preparation.

10.3.3 Sodium Carbonate (Na_2CO_3) Inorganic Carbon Stock Solution (100mg/L C): Add 0.882g of Sodium Carbonate to a 1Lvolumetric containing 500mL of DI water. This solution is to be mixed and brought to final volume with DI water.

10.4 Standard Solutions

10.4.1 10mg/L LCS/ICV solution: In a 50mL volumetric flask add 0.5mL of secondary stock standard and dilute to 50mL with DI water. This solution may be used for 1 month from preparation.

10.4.2 25 mg/L CCV solution: In a 100mL volumetric flask add 2.5mL of the primary stock solution and dilute to 100mL with DI water. This solution may be used for 1 month from preparation.

10.4.3 Matrix Spike (true value= 10mg/L): In a 50mL volumetric flask add 0.5mL of secondary stock standard (1000mg/L) and dilute to volume with sample.

10.4.4 Inorganic Carbon Efficiency (TV= 10mg/L): In a 50mL volumetric flask add 5.0mL of 100mg/L Inorganic standard and dilute to 50mL with sample.

11. Calibration

11.1 A calibration curve must be prepared every 6 months or when QC recoveries fail.

11.2 Prepare a series of standards by pipetting the volumes of Potassium Hydrogen Phosphate (indicated in the table below), from the primary Stock solution, into 100mL volumetric flasks. Dilute each sample to volume with DI water.

mL of Standard 1000 mg/L KHP	Concentration (mg/L)
0.0	0
0.1	1
1.0	10
2.5	25
5.0	50
7.5	75
10.0	100

Pour the standards into 40mL VOA vials and place the vials into positions 1-6 on the autosampler.

11.2.1 Click on the TOC icon

11.2.2 Click EDITOR

11.2.3 Click SEQUENCE

11.2.4 Click NEW

11.2.5 Name the File mmddyrcal (i.e, 02272008cal for a calibration analyzed on February 27, 2008).

11.2.6 Click SAMPLE TYPE: choose clean-up

11.2.7 Under Method primary choose: default clean-up method

11.2.8 Click OK at the bottom of the screen

11.2.9 Click ADD/INSERT

11.2.10 Click SAMPLE TYPE: choose sample

11.2.11 Under Method primary choose the method 5310 C

11.2.12 Sample ID type in blank

11.2.13 Select OK

11.2.14 Click Add/Insert

11.2.15 Click SAMPLE TYPE CAL

11.2.16 Under Method primary, select method 5310 C or 9060/9060A

11.2.17 Click OK

11.2.18 Save tray

11.2.19 Click on MONITOR

11.2.20 Click on SEQUENCE

11.2.21 Load Active Sequence

11.2.22 Select new Calibration tray

11.2.23 Click the GREEN ARROW on the bottom left of the page

11.3 To view and process the new curve:

11.3.1 Click on the PC APPLICATION tab

11.3.2 Click on the REPORTER TAB

11.3.3 User name and password is toc

11.3.4 In the Instrument box, choose F750730374-Wet Chemistry

11.3.5 Click on the Picture of the Calibration Curve (top left)

11.3.6 Right click on the CALIBRATION RUN

11.3.7 Click VIEW CALIBRATION

11.3.8 Click on the TOC tab (top middle)

11.3.9 Click on the printer icon above the curve (this will **print** a copy of the calibration curve). Click on the printer icon on the top left hand corner. This will **print** the concentrations of the curve.

11.3.10 The r^2 must be ≥ 0.99 (or r ≥ 0.995) before samples can be analyzed using the calibration.

12. Procedure

12.1 Click on the TOC icon

12.2 Click on DEVICE APPLICATION

12.3 Username and password is toc

12.4 Click on CONFIGURATION

12.5 Click on SYSTEM

12.6 Click on AUTOMATED START UP/SHUT DOWN

12.7 Click the WAKE UP TAB to start the nitrogen flowing through the system. THE PURGE CONDITIONS ARE PROGRAMMED INTO THE INSTRUMENT'S SOFTWARE.

12.8 Click on EDITOR

12.9 Click SEQUENCE

12.10 Click NEW

12.11 Name the File mmddyr (i.e., 02272008)

12.12 Click SAMPLE TYPE : choose clean-up

12.13 Change the replicates to 4

12.14 Method primary choose: default clean-up method

12.15 Click OK at the bottom of the screen

12.16 Click ADD/INSERT

12.17 Click SAMPLE TYPE: choose sample. Type in the total number of samples and QC to be analyzed.

12.17.1 For Standard Method 5310 C samples must be analyzed in duplicate.

12.17.2 For EPA Method 9060/9060A: sample must be analyzed in quadruplicate.

12.18 Method primary choose method 5310 C or 9060/9060A.

12.19 Sample ID type in 1 and select use incrementer

12.20 Select OK

12.21 Type in the sample numbers on the main screen

12.22 Sample 1 should be a CCV, sample 2 should be the LCS/ICV, and sample 3 should be the MBLK. Analytical samples follow.

12.23 For QC samples be sure to check std #2 for the 10mg/L LCS/ICV and check standard #3 for the 25mg/L **CCV** on the main screen.

12.24 The ending QC must be the same as the beginning QC.

12.25 Save tray

12.26 Click on MONITOR

12.27 Click on SEQUENCE

12.28 Load Active Sequence

12.29 Select new Calibration tray

12.30 Click the GREEN ARROW on the bottom left of the page

12.31 To process the new tray:

12.31.1 Click on the PC APPLICATION LAB

12.31.2 Click on the REPORTER TAB

12.31.3 User name and password is toc

12.31.4 In the Instrument box choose F750730374-Wet Chemistry

12.31.5 Right click on the RUN ID

12.31.6 Choose ADD SAMPLE TO WORK LIST

12.31.7 Click on TOC tab

12.31.8 When the tray is done, print the report

13. Calculations

13.1 Sample Concentration calculation

13.1.1 $$Conc(mg/L) = \frac{(A_s - A_{RB}) * RF}{SA * 1000}$$

Where:

A_S = area of the sample
A_{RB} = area of the sample
RF = response factor from the curve
SA = sample volume analyzed (e.g., 2mL)
1000= unit conversion factor

13.2 Standard Concentration calculation

13.2.1 $$Conc(mg/L) = \frac{(A_S - A_{RW}) * RF}{SA * 1000}$$

Where:

A_S = area of the sample
A_{Rw} = area of the reagent water
RF = response factor from the curve
SA = sample volume analyzed (e.g., 2mL)
1000 = unit conversion factor

13.3 Reporting results

13.3.1 Standard methods 5310C results are reported as the average between the 2 replicates.

13.3.2 EPA Method 9060/9060A must be reported as the average of the four results and the range of the results.

14. Quality Control

14.1 A method blank must be analyzed with each batch of 10 samples.

14.2 An LCS/ICV must be analyzed with every batch of 10 samples. Acceptance limits are 85% -115%. ICV/LCS is from a second source.

14.3 Duplicate sample

14.3.1 Standard Method 5310 C: must be analyzed with each batch of 20 samples.

14.3.2 EPA Method 9060: must be analyzed with each batch of 10 samples.

14.3.3 The acceptance limit for both methods is 20%. RPD.

14.4 Matrix Spike Sample

14.4.1 Standard Method 5310 C: must be analyzed with each batch of 20 samples.

14.4.2 EPA Method 9060/9060A: must be analyzed with each batch of 10 samples.

14.4.3 The acceptable limit for both methods is 85% -115 % Recovery.

14.5 A CCV must be analyzed with each batch of twenty samples. The acceptance limit is 90-110% Recovery.

14.6 Inorganic Carbon Efficiency must be analyzed with each batch of 20 samples for Method 5310 C. The acceptance limit is 75-125 % Recovery. One sample per matrix and per QC batch must be spiked with inorganic carbon to determine the efficiency of the inorganic carbon removal process. To perform this check, split a sample into two portions and spike one portion with the inorganic carbon spike. Analyze both samples and calculate and record the percent recovery. There should not be any inorganic carbon recovered in the spiked portion of the sample. If inorganic carbon is recovered, adjust sample container, sample volume, pH, purge gas flow rate and/or purge time to obtain complete removal of inorganic carbon. Include the results for the inorganic spike with the raw data; however, do not report this result.

14.7 Sample replicates must be within 10% RPD.

14.8 Corrective Actions for Out-Of-Control Data

14.8.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.8.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.8.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are noted in the final report.

14.8.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS

results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.8.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.8.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.8.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.8.5.2 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their reporting limit, and duplicate precision meets the acceptance criteria.

14.8.6 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 Each analyst must read, understand, and agree to follow this procedure with written documentation maintained in their training file.

15.2 Acceptable method performance shall be verified regularly by analyzing performance evaluation samples. These samples are obtained from independent sources and analyzed as a part of the normal sample workload.

15.3 Each analyst must complete an initial demonstration of capability (IDOC) study. Documentation of the IDOC is maintained on file in each analyst's training file.

15.4 The MDL is verified annually.

15.5 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.6 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.7 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.8 LOD and LOQ (See table below.)

LOQ	1.0mg/L		
LOD (or MDL) 5310C	0.157mg/L	Effective 7-13-2013	LOD is subject to change
LOD 9060	0.116mg/L	Effective 11-1-2012	LOD is subject to change

16. Pollution Prevention and Waste Management

16.1 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in Pace Analytical's Chemical Hygiene Plan and in the SDSs.

17. References

17.1 Standard Methods for the Examination of Water and Wastewater, Method 5310 C, 20th Edition, 1998.

17.2 Standard Methods for the Examination of Water and Wastewater, Method 5310 C, 2000.

17.3 USEPA, SW-846 III Ed., Method 9060, Total Organic Carbon, September 1986.

17.4 USEPA, SW-846 Final Update IIIB, Method 9060A, Total Organic Carbon, Revision 1, November 2004.

17.5 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.6 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.7 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 None

19. Deviations from Promulgated Methods.

19.1 Method 9060A section 7.3 states to purge the sample for 10 minutes. The sample is purged for 2 minutes as per manufacturer instructions.

20. Revisions

Document No.	Reason for Change	Date
PGH-I-060-3	1. Annual Review (2011): Updated Cover Sheet, Headers and Footers for this Revision, Added Signature line for Department Supervisor/Manager, Added Annual Review Signature lines (no changes) 2. Added Section 18: Tables, Diagrams, Flowchart, Appendices, etc. 3. Added Revisions Section (Section 19)	23May2011
PGH-I-060-4	1. Method 9060A was added 2. Added a table of contents 3. RL was added to section 2.1 4. Changed the Initial QC order in Section 12.22 5. Added method 5310C results are reported as an average value in section 13.3.1. 6. Added comments on the Inorganic Carbon Efficiency for Method 5310C in section 14.6. 7. Added MDL is verified yearly in section 15.4. 8. Added Method Deviation section 20 9. Added LOQ/LOD section 15.	19Jun2013
PGH-I-606-5	1. General editing for grammar and spelling. 2. Document Reformatted.	27Jun2014

Document No.	Reason for Change	Date
PGH-I-606-6	Added section 19.1: Method 9060A section 7.3 states to purge the sample for 10 minutes. The sample is purged for 2 minutes as per manufacturer instructions	19Dec2014

STANDARD OPERATING PROCEDURE

Filterable Residue (Total Dissolved Solids), SM 2540 C-1997

SOP NUMBER:	PGH-I-020-9
REVIEW:	Tim Harrison and Brayan Hampton
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-I-020-8
REVIEW DATE:	Upon Procedural Change

APPROVALS

Assistant General Manager	5/31/14 Date
Senior Quality Manager	7/11/14 Date
Department Manager/Supervisor	7/11/14 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

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TABLE OF CONTENTS

1. Purpose

   1.1 This Standard Operating Procedure (SOP) documents the procedure to be used for the determination of Filterable Residue or Total Dissolved Solids (TDS) per method SM 2540 C-1997.

2. Scope and Application

   2.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

   2.2 The practical range of the determination is 10mg/L to 20,000mg/L. The Reporting limit is 10mg/L.

3. Summary of Method

   3.1 A well-mixed sample is filtered through a glass fiber filter. The filtrate is collected, evaporated in an oven and then transferred to the 180°C oven and the evaporated sample is dried to constant weight at 180°C.

   3.2 If Non-Filterable Residue (Total Suspended Solids or TSS) is also being determined, the filtrate from that method may be used to determine the Filterable Residue (TDS).

4. Interferences

   4.1 Residues from highly mineralized waters that contain significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

   4.2 Samples that contain high concentrations of bicarbonate will require careful, and possibly prolonged, drying at 180°C to insure that all the bicarbonate is converted to carbonate.

   4.3 Significant amounts of residue in the evaporation dish can crust over and may entrap water that will not be driven off in the drying process. The total amount of residue should be limited to about 200mg.

5. Safety

   5.1 All samples should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. At a minimum, gloves, safety glasses, and a lab coat must be worn when performing this procedure.

   5.2 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

   5.3 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

   5.4 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

   6.1 Filterable Residue – Those solids capable of passing through a glass fiber filter and dried to a constant weight at 180°C.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Samples may be collected in either glass or plastic bottles.

8.2 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

8.3 Preservation: Samples must be cooled to 4±2^{o}C to after collection and maintained at that temperature until analysis.

8.4 Shipment: Samples are to be shipped in a container packed in enough ice filled to maintain a temperature of 4±2^{o}C.

8.5 Storage: Samples are stored at 4±2°C minimize microbiological decomposition of solids.

8.6 Holding time: Sample must be analyzed within 7 days of sample collection.

9. Equipment and Supplies

9.1 47mm glass fiber filter discs, without organic binder.

9.2 Filter holder, membrane filter funnel.

9.3 500mL filter flask.

9.4 150mL porcelain evaporating dishes.

9.5 Drying oven, ~100°C ± 20°C.

9.6 Drying oven, 180 ± 2°C.

9.7 Desiccator and desiccant.

9.8 Analytical balance, capable of weighing to 0.1 milligrams (mg).

10. Reagents and Standards

10.1 Solids Standard: Dissolve 1.0000g of KCl in a 1L volumetric flask containing approximately 800mL of DI water. Dilute to volume with DI water. Invert to mix. Final concentration = 1000mg/L.

11. Calibration

11.1 The calibration of the balance used for the solids determination must be verified prior to, and at the conclusion of the weighing of any samples in order to bracket the measurements.

11.1.1 Additional verifications during the weighing process are recommended.

11.2 The temperature of the drying oven must be verified at a minimum of once per day, prior to the drying of any samples.

12. Procedure

12.1 Allow the samples to warm to room temperature.

12.2 Preparation of evaporating dishes: Dry and clean the evaporating dishes in a muffle furnace at 550°C ± 50°C for one hour. Remove the dishes from the furnace and allow them to cool in a desiccator. Store the dishes in the desiccator until needed. Weigh the evaporating dish before filtering the sample.

12.3 Assemble the filter apparatus and apply the vacuum.

12.3.1 Preparation of the glass fiber filter: Place the filter, with wrinkled side up, on the membrane filter apparatus. While the vacuum is applied, rinse the filter with three successive 20mL aliquots of DI water. Continue to apply the vacuum until all visible traces of water have been eliminated. Discard the rinses.

12.4 Shake the sample vigorously and rapidly measure the appropriate aliquot of sample into a graduated cylinder.

12.5 Pour the sample into the filter funnel and allow the sample to pass through the glass fiber filter.

12.6 Rinse the filter three times with 10mL portions of DI water and continue to apply vacuum for about 3 minutes after the filtration is complete to remove as much water as possible.

12.7 Transfer the filtrate to a weighed evaporation dish and evaporate to dryness in an oven at approximately100°C.

12.8 Remove the dish from the first oven and transfer it to the 180 ± 2°C oven and allow it to dry:

12.9 Drying Option 1:

12.9.1 Dry the evaporation dish for at least sixteen (16) hours at 180° ± 2°C.

12.9.1.1 Record the date and time that the filter discs are placed into the oven and removed from the oven on the bench sheet.

12.9.1.2 Record, the temperature of the oven immediately before the samples are placed into the oven and immediately prior to the removal of the samples from the oven on the bench sheet.

12.9.2 Remove the evaporation dish from the drying oven and place it in a desiccator to cool for a minimum of one (1) hour.

12.9.3 Weigh the evaporation dish and record the information on the bench sheet.

12.10 Drying Option 2:

12.10.1 Dry the evaporation disk in the 180 ± 2°C oven for 1 hour.

12.10.1.1 Record the time that the filter is placed into the oven and removed from the oven on the bench sheet.

12.10.1.2 Record, the temperature of the oven immediately before the samples are placed into the oven and immediately prior to the removal of the samples from the oven on the bench sheet.

12.10.2 Weigh the dish containing the sample residue to a constant mass.

12.10.2.1 Weigh the dish containing the sample residue on an analytical balance and record the mass on the bench sheet.

12.10.2.2 Repeat the drying cycle until the mass difference between two consecutive measurements is less than 0.5mg.

12.11 At the conclusion of the final weigh backs, the balance calibration must be re-verified using a single certified reference weight. The results of the verification are to be documented on the laboratory bench sheet.

13. Calculations

13.1 Calculate Filterable Residue as follows:

$$Filterable\_residue\,(mg/L) = \frac{A-B}{C} \times 1000$$

Where

A = mass of dried residue and dish in mg
B = mass of dish in mg
C = volume of sample analyzed in mL

14. Quality Control

14.1 A method blank of DI water must be analyzed with each batch of samples.

14.1.1 The method blank must not be greater than the reporting limit (RL).

14.2 A Laboratory Control Sample (LCS) must be analyzed with each sample batch. The percent amount of recovery must not exceed ±15%.

14.3 One duplicate (DUP) sample must be analyzed per every 10 samples in the batch.

14.3.1 The duplicate determinations should agree within 5% of their average mass.

14.4 Assessment and acceptance criteria for the QC samples

14.4.1 If the Method Blank (MB) is greater than the reporting limit, evaluate the cause and correct.

14.4.2 If the LCS is outside of the acceptance criteria, reanalyze all associated samples.

14.4.3 If the Relative Percent Difference (RPD) for the duplicate is greater than ±20%, reanalyze all associated samples.

14.5 If the balance calibration verification performed at the conclusion of the weigh backs is not within the established acceptance range, the analyst shall initiate a corrective action to determine the cause of the problem.

14.5.1 Appropriate steps shall be taken to correct the problem and to demonstrate that the balance is within acceptable limits.

14.5.1.1 All of the samples will be re-weighed, and bracketed with a verification using a certified weight at the end.

14.5.1.2 If the cause cannot be determined, the balance will be taken out of service and the samples will be re-weighed on a different calibrated balance.

14.5.1.3 The balance will not be returned to service until the cause of the problem is determined and verified to be back within the acceptable limits using certified weights.

14.5.1.4 All records of service and maintenance shall be documented in the balance logbook.

14.5.1.5 Corrective actions will be documented in LabTrack.

14.6 Corrective Actions for Out-Of-Control Data

14.6.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.6.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.6.3 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.6.3.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.6.4 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 The requirements that must be met include but not limited to: the reading and understanding the method and SOP, analysis of MDLs and performance evaluation samples, and the analysis of in-house laboratory quality control samples.

15.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Pollution prevention encompasses any techniques that reduces or eliminates the quantity or toxicity of waste at the point of generation.

17. References

17.1 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.2 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.3 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.4 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Method 2540C, 1995.

17.5 Standard Methods for the Examination of Water and Wastewater, Method 2540 C-1997.

18. Appendices

18.1 Attachment No. 1: TDS Bench Sheet (Example).

19. Method Modifications

19.1 Section 12.9: Dry the evaporation dish for at least sixteen (16) hours at 180+/- 2°C.

20. Revisions

Document Number	Reason for Change	Date
PGH-I-020-8	1. Updated cover page, headers and footers for this revision. 2. Added copyright footer to the cover page. 3. Added Table of Contents. 4. Sections 12.8-12.10: added ±2°C requirement to 180°C oven temp. 5. Section 12: Added temperature documentation requirements for oven. Record on the bench sheet, the temperature of the oven immediately before the samples are placed into the oven and immediately prior to the removal of the samples from the oven. 6. Section 17: Added TNI Standard reference, removed EPA 160.1 reference (retired by MUR). Updated references.	17Jan2014
PGH-I-020-9	1. Cover and Sections 1.1 and 17.4: updated method references per latest MUR. 2. General: made editorial corrections. 3. Document Reformatted. 4. Updated spread sheet as Attachment No 1	31May2014

Attachment No. 1 - TDS Bench Sheet (Example)

Residue Determinations

Non-Filterable (TDS) Method Number: 2540 C

	Initials:	Date:
Tested by:	-	-

Balance: Sartorius BA2105

Balance Calibration Check

True	Actual	Pass
50.0g	-	No

*Actual Value must be between 49.5g and 50.5g

	First Drying In	First Drying Out	Second Drying In	Second Drying Out
Oven Temperature	-	-	-	-
Oven Times		-	-	-
Dessicator Times	-	-	-	-

Worksheet: -
Batch -
HBN: -
Start Time: -

Det. Lim: <10 Oven #10: 105C Oven #3 : 180C 1ST READING 2ND READING

Tare ID	PROJ #	SAMPLE ID	Sample VOL (mL)	CRUCIBLE WEIGHT (g)	CRUCIBLE & RESIDUE (g)	CRUCIBLE & RESIDUE (g)	DIFFERNCE IN READINGS (g)	RES. (mg/L)	Raw Conc. (mg/L)
ICB	-	-	-	-	-	-	NA	#DIV/0!	0.0
LCS	-	-	-	-	-	-	NA	#DIV/0!	0.0
1	-	-	-	-	-	-	NA	#DIV/0!	0.0
2	-	-	-	-	-	-	NA	#DIV/0!	0.0
3	-	-	-	-	-	-	NA	#DIV/0!	0.0
4	-	-	-	-	-	-	NA	#DIV/0!	0.0
5	-	-	-	-	-	-	NA	#DIV/0!	0.0
6	-	-	-	-	-	-	NA	#DIV/0!	0.0
7	-	-	-	-	-	-	NA	#DIV/0!	0.0
8	-	-	-	-	-	-	NA	#DIV/0!	0.0
9	-	-	-	-	-	-	NA	#DIV/0!	0.0
10	-	-	-	-	-	-	NA	#DIV/0!	0.0
DUP	-	-	-	-	-	-	NA	#DIV/0!	0.0
11	-	-	-	-	-	-	NA	#DIV/0!	0.0
12	-	-	-	-	-	-	NA	#DIV/0!	0.0
13	-	-	-	-	-	-	NA	#DIV/0!	0.0
14	-	-	-	-	-	-	NA	#DIV/0!	0.0
15	-	-	-	-	-	-	NA	#DIV/0!	0.0
16	-	-	-	-	-	-	NA	#DIV/0!	0.0
17	-	-	-	-	-	-	NA	#DIV/0!	0.0
18	-	-	-	-	-	-	NA	#DIV/0!	0.0
19	-	-	-	-	-	-	NA	#DIV/0!	0.0
20	-	-	-	-	-	-	NA	#DIV/0!	0.0
DUP	-	-	-	-	-	-	NA	#DIV/0!	0.0

LCS ID: -
LCS Recovery
#DIV/0!
DUPLICATE RPD

sam id	-
sam res	#DIV/0!
dup result	#DIV/0!
RPD	0%
sam id	-
sam res	#DIV/0!
dup result	#DIV/0!
RPD	0%

Sample ID -
Sample ID -

Repeat drying cycle until a constant weight is obtained (weight loss is less than 0.0005 g/L)

Observations: -
-
-

"-" indicates no data to fill this cell.

WC030-1(16April2006)

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STANDARD OPERATING PROCEDURE

PREPARATION AND ANALYSIS OF SAMPLES FOR THE DETERMINATION OF DIOXINS AND FURANS

Reference Methods: USEPA Method 8290/8290A/1613B/DLM2.0

Local SOP Number:	S-MN-H-001-Rev.26
Effective Date:	Date of Final Signature
Supersedes:	S-MN-H-001-Rev.25

APPROVALS

Laboratory General Manager — Date: 11Sep2015

Laboratory Quality Manager — Date: 11Sep2015

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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SECTION **PAGE**

1. Purpose/Identification of Method

1.1. The purpose of this standard operating procedure is to describe the preparation, analysis, processing, and reporting of samples for the determination of dioxins and furans using USEPA Method 8290, 8290A, 1613B and DLM2.0.

2. Summary of Method

2.1. Stable isotopically labeled analogs of 15 of the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are added to each sample. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Water samples are extracted in separatory funnels or by solid phase extraction. Soils and other finely divided solids are extracted using Soxhlet or microwave assisted extraction apparatus. Note that, in this document, CDD and CDF mean chlorinated dibenzo-p-dioxin and chlorinated dibenzofuran. The prefixes to those acronyms are P for poly, T for tetra, Pe for penta, Hx for hexa, Hp for hepta and O for octa.

2.2. After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanup may include back extraction with acid and/or base, alumina, silica gel, and activated carbon chromatography.

2.3. Samples are spiked with two labeled recovery standards that are used to determine the portion of the analytes and internal standards that survived the extraction and enrichment processes. The extracts are then analyzed using high resolution gas chromatography/high resolution mass spectrometry to determine the concentration of PCDDs and PCDFs present in the samples.

2.4. The accuracy of the method can be affected by matrix interferences, especially for non-isotope dilution analytes.

2.5. Pace Analytical will comment all deviations from the SOP in the final narrative to be included with each project. Generally, deviations that are not specifically addressed in the SOP will trigger a re-extraction. Exceptions will generally only be allowed after discussion with the client.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. **Parameter**s: This SOP applies to the dioxin and furan compounds listed in Attachment IV.

4. Applicable Matrices

4.1. This SOP is applicable to water, sludge, soil, fly ash, tissue, food/food oil and waste materials. This method can be applied to most other matrices as well.

Note: Per Ohio VAP OAC Rule 3745-300-01 (A) this method applies to “environmental media”, including soil, sediment, surface water, and ground water. Environmental media also include naturally occurring transitional zones between soil, sediment, surface water or ground water, such as bedrock, soil gas, and air.

5. Limits of Detection and Quantitation

5.1. The reporting limits (LOQ) for all analytes for this method correspond to the concentration of the CS-1 (0.5-5 pg/uL) and are calculated based on the amount of sample used for the determination. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1. Most samples analyzed for PCDD/PCDF content contain other organic compounds that interfere with or contaminate the mass spectrometric instrumental system. Therefore, after initial extraction, extracts

are taken through the cleanup steps outlined in the "Extract Enrichment/Clean Up" section of this procedure. Exceptions to performing the optional clean up steps of acid/base and carbon column cleanup steps may be made with consultation of the laboratory manager and are usually limited to water matrices. The acid clean-up procedure is used to remove lipids in tissue samples and must not be omitted for this matrix.

6.2. Matrix interferences may be caused by contaminants (particularly chlorinated biphenyl ethers) co-extracted from the sample and vary considerably from source to source. These biphenyl ethers rearrange in the mass spectrometer source to form dibenzofurans.

6.3. Some samples may contain levels of interfering compounds that overload the analyte clean up columns. Consult the laboratory manager for alternate procedures should this occur.

6.4. Rigorous glassware cleaning techniques must be used and method blank data must be monitored to evaluate the effectiveness of the glassware cleaning techniques.

6.5. HPLC grade solvents must be used for extractions. Solvents having new lot numbers must be screened for contamination prior to use by analyzing a solvent blank by the applicable analytical methods.

6.6. Raw data from all blanks, samples, and spikes are evaluated for interferences. Determine if the source of interferences is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

6.7. If chromatographic interferences are present (specifically, matrix components that interfere with the determination of PCDDs or PCDFs), the area from the least affected signal of the pair is used along with the theoretical ratio to determine the area of the second ion. These values are then used to calculate the estimated maximum concentration that is then reported as the estimated maximum possible concentration (EMPC).

6.8. Some interference may be reduced by analysis of a dilution of the extract.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Table 7.1 – Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Glass container (see section 7.2). One liter of water samples containing less than or equal to 1% solids should be extracted. Reduced/elevated volumes are used when high level samples are anticipated or to match project requirements. Aqueous or solid samples containing greater than 1% solids must be considered as solids.	If residual chlorine is present, 80 mg of sodium thiosulfate is typically added to the sample at the time of collection to neutralize the chlorine.	Maintain samples at <6°C under darkness from the time of collection until extraction.	See section 7.4.
Solid	Glass container (see section 7.2). Sufficient volume is typically extracted to provide a dry weight of 10 grams (except for tissue samples and other samples noted to be reported on an as received basis).	n/a	Maintain samples at <6°C under darkness from the time of collection until extraction. WI samples must be frozen ≤-10°C	See section 7.4.
Tissue	Glass container (see section 7.2).	n/a	Stored frozen at ≤-10°C under darkness.	See section 7.4.

Oil	Glass container (see section 7.2). One hundred milligram aliquots are typically used for waste oil-based samples. Twenty-gram aliquots are typically used for food oil samples.	n/a	Maintain samples at <6°C under darkness from the time of collection until extraction.	See section 7.4.

7.2. Sample bottles - 1 Liter glass amber bottles for liquids that contain less than 1% solids; 500 milliliter (mL) wide mouth (or smaller) glass amber bottles for solid and sludge. All bottles are purchased pre-cleaned from the vendor. If glass amber bottles are not available, samples must be protected from the light. All bottles should have Teflon lined caps. Laboratory cleaned bottles may be substituted for pre-cleaned bottles. Bottles should be detergent washed, then solvent rinsed and baked at 450°C for the minimum of one hour.

7.3. One gram or smaller aliquots are typically extracted for waste samples and samples suspected to contain high analyte levels. Sample amounts extracted for food samples containing fat are typically based on the lipid content of the sample. Non-fat foods and all feeds are based on the raw sample weight.

7.4. For method 8290 and 8290A, samples are typically extracted within 30 days of sample collection and the extract analyzed within 45 days of extraction. For DLM, shorter hold times apply, see Attachment VIII. For Method 1613B, samples are typically extracted within one year of sample collection and the extract analyzed within 40 days of extraction. Some states have implemented shorter extraction hold times. Exceeding hold times between collection and extraction or extraction and analysis do not necessarily invalidate the results. Whenever samples are analyzed after the holding time expiration date, the results must be considered to be minimum concentrations and identified as such.

7.5. All sample extracts are stored in the extract freezer at <-10 °C until analysis. Extracts are warmed to room temperature and vortexed before analysis.

7.6. Criteria for Acceptance/Rejection of Samples

7.6.1. Samples are to be rejected if information allowing determination of the applicable test and client information cannot be obtained.

7.6.2. If sample integrity has been compromised, the client must be contacted for instructions and permission to proceed with analysis. The client's comments and instructions are documented as part of routine laboratory policy.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Table 9.1 – Equipment and Supplies

Description	Supply	Fisher, or Equivalent
Solvent	Acetone - Optima (4bottle/cs)	A929-4
Solvent	Methanol - Optima (4bottle/cs)	A454-4
Solvent	N-Nonane, 99% 100mL	AC129111000
Solvent	N-Tridecane, 99+% 100mL	AC139511000
Acid	Sulfuric Acid 2.5L (6bottle/cs)	A300S-212
Solvent	Hexane, Ded. Lots (4bottle/cs)	H306-4
Solvent	Me.Chloride, Ded. Lots (4bottle/cs)	D151-4
Solvent	Toluene, Ded. Lots (4bottle/cs)	T291-4
Acid	GW: Nitric Acid (6bottle/cs)	A509P212
Solvent	Ethyl Ether Annhydrous 1L	EI38-1
Solvent	HPLC Grade Cylcohexane	C620-1
Solvent	HPLC Grade Iso-Octane	

Sodium Thiosulfate	Used to treat residual chlorine	Fisher Scientific or equivalent replacement
Dispenser	25-100ml dispenser for SF	13-688-75
Containers	12 dram Vials (3 pk/cs)	03-339-26H
Containers	250 mL Disp. Glass Jars (24jar/cs)	NC9199987
Containers	40mL Clear Vial w/cap (80vial/cs)	NC9879693
Containers	500mL Glass Jar (12jar/cs)	NC9941118
Containers	8oz. Clear Centrifuge Jar (96JARS/CS))	NC0475499
Containers	Bottle 1L amber (12bottle/cs)	05-719-91
Containers	DW: 60mL Clear Vial (72vial/cs)	05-719-398
Containers	GW: Versa-Clean (12bottle/cs)	04-342
Containers	12ml Standard Vials	03-340-60c
Containers	200ml Kimble Chase Kimble Vol Flask	10-212C
Funnels	Case of 300ml Buchner Funnels	10-358-22L
Funnels	250 ml Funnel for SPE (47mm)	13-645-089
Funnels	1000 ml Funnel for SPE (47mm)	13-645-090
Beakers	Polypropylene Disp. 250ml beakers (lipids)	01-291-5
Syringes	50ml Syringe DISP. For Silica and Alumina	1481736
Syringes	25ml Syringe DISP for DW Silica	148268
Containers	Vials with insert for 8280	03-376-407
Containers	Amber jars for Silica Media	NC9941126
Containers	2L C and G containers- for TIP WASTE	NC9204036
Centrifuge tubes	50ml centrifuge tubes	06-0443-18
Cleaning	GW: Acetone - Hist. 20L saftin	A16S-20
	hawkins Sodium Bicarbonate	14422
	Chromerge	C577-12
	Bin for glassware cleaning, select color	60086
	Lid for Bins	60962
Extraction	Whatman Thimbles - L 43X123mm 25/pk	09-656H
	Sand - QC Standard Ottawa 2.5KG	SX0075-3
	PTFE Boiling Stones - 450g	09-191-20
	Round Botton standalone 500mls	07-250-079
	Tongue Depressors 6in by 3/4in	11-700-556
	Soxhlet extraction apparatus	Fisher Scientific or equivalent
	Microwave Extraction System	CEM MARS 5
	Heating Mantles for Soxhlet apparatus	Fisher Scientific or equivalent
	Dean Stark Apparatus	K585151-0035
	1000ml Separatory Funnel with Teflon stop cocks	Fisher Scientific or equivalent
Cleanup	Glass Wool, silane treated, Supelco	2-0411
	Celite, Supelco	20199-U
	Glass Tubing 12mm X 4ft	11-362G
	Glass Tubing 20mm X 4ft	11-362N
	Glass Tubing 15mm X 4ft	11-362J
	Alumina (50-200 mesh) ICN	NC9983739
	Silica Gel (100-200mesh) 2.5kg	S679-212
	Glass Wool - Regular 1lb	11-388
	3 chamber snyder column	NC9207667
	Sodium Sulfate Annhydrous	S415-200LB
	Florisil, 60-100 mesh/Reagent Gr.	220752-1KG
Pippetters	10uL Tips(10pk/cs)	13-707-64
	Monstr-Pipette (8pk/cs)	22-378893
	Pipet - Disp. 5 3/4" (4box/cs)	13-678-20B

	Pipet - Disp. 9" (4box/cs)	13-678-20D
	Tips 0-200 uL	02-681-135
	50-1000 tipsuL	222491954
	Bulbs for Small Pipettes (2.25inch)	03-448-22
	Bulbs for Small Pipettes (1.5inch)	03-448-21
Needles	N Evap needles	NC9433071
Filters	DW: Glass Fiber Filter (100/pk)	09-873DD
Funnels	Funnel - 60mm Disposable (100/cs)	05-555-6
	Large POWDER FUNNEL 110-150 4/PK	10-500-3
	Funnels - Disp. Powder for H2Os (36/cs)	10-500-1
Balance	0.01g and 0.0001g	Fisher Scientific or equivalent
Drying oven	Up to 400 degrees C	Fisher Scientific or equivalent
Centrifuge	For samples in extraction lab	Fisher Scientific or equivalent
Avalon	Data Processing System for HRMS	
Capillary Column	DB 225 30m 0.25mm ID 0.25u	J&W
Capillary Column	DB 5 60m 0.25mm ID 0.25u	J&W
HRMS	High Resolution Mass Spec equipped with a GC HP Agilent 6890 or equivilant	Auto Spec or equivialent
Avalon	Data processing and reporting software	Avalon, see master software list for current version

10. Reagents and Standards

10.1. Table 10.1 – Reagents and Standards

Reagent/Standard	Concentration/Description	Requirements/Vendor/Item #
Acidic Silica gel	30% w/w, thoroughly mix 44.0g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.	Fisher Scientific or equivalent
Basic Silica gel	Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw cap.	Fisher Scientific or equivalent
Canola oil	Canola oil, or equivalent, for Oil quality control sample matrix,	Local grocery store
Primary Ical Stock Standard		
ICV Stock Standard		

10.2. Table 10.2 - Working Standard Dilutions and Concentrations

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration
Sodium hydroxide (NaOH)	40 g	Reagent water	~1 L	1 L	1N
Potassium Phosphate, monobasic (KH_2PO_4)	68.05 g	Reagent water	~1 L	1 L	0.5 M

10.3. Standards and working solutions are prepared from or compared to certified standards or purchased as certified premixed standards. All standards are valid for 1 year from date opened (or prepared). All standards are stored per manufacturer instructions until opened. Opened standards are stored in glass bottles at <6°C. The standards must be stored at any refrigerator or freezer temperature (not to exceed

6°C) sufficient to maintain standard/solvent volume for nonane or tridecane. Standards may be re-verified by comparison to a valid native analyte solution. The final concentrations determined for any solution being re-verified must be within 20% of the expected concentrations for that solution.

10.4. The preparation of standards and working solutions is thoroughly documented in the appropriate standards notebook. Such documentation allows the traceability of each solution to a certified, purchased solution.

10.5. Preparation of Primary Stock Solution of Internal Standards

NOTE: Identification # denotes the next sequential number assigned to the vial upon receipt in the Dioxin Stock Standard Tracking Logbook.

Compound	Conc (mircrogram/milliliter (µg/mL))
2,3,7,8-TCDD-$^{13}C_{12}$	1.0
2,3,7,8-TCDF-$^{13}C_{12}$	1.0
1,2,3,7,8-PeCDD-$^{13}C_{12}$	1.0
1,2,3,7,8-PeCDF-$^{13}C_{12}$	1.0
2,3,4,7,8-PeCDF-$^{13}C_{12}$	1.0
1,2,3,4,7,8-HxCDD-$^{13}C_{12}$	1.0
1,2,3,6,7,8-HxCDD-$^{13}C_{12}$	1.0
1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,6,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,7,8,9-HxCDF-$^{13}C_{12}$	1.0
2,3,4,6,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,4,6,7,8-HpCDD-$^{13}C_{12}$	1.0
1,2,3,4,6,7,8-HpCDF-$^{13}C_{12}$	1.0
1,2,3,4,7,8,9-HpCDF-$^{13}C_{12}$	1.0
OCDD-$^{13}C_{12}$	2.0

10.5.1. All compounds must be purchased in nonane or equivalent (Cerilliant or equivalent).

Note: A stock solution containing labeled PCDDs and PCDFs at concentrations of 1.0 nanogrom/microliter (ng/uL) (2.0 ng/µL for OCDD-$^{13}C_{12}$) is available from CIL or Wellington Laboratories. This solution may be diluted 10x to prepare the secondary solution described below.

10.5.2. Vortex the vial for at least 1 minute after bringing to room temperature.

10.5.3. After sonication, pipette the compounds noted above into a pre-rinsed 2 dram vial and label. Identification must include: ID# and log #, $^{13}C_{12}$ primary stock solution of internal standard, preparation date, expiration date and preparer's initials.

10.5.4. Seal vial with Teflon tape and store in standards freezer at-18°C ± 2°C.

10.5.5. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.6. Preparation of Internal Standard Spiking Solution

10.6.1. Allow the stock standard to reach room temperature before using. Vortex for ~10 seconds before taking an aliquot.

10.6.2. Using an Eppendorf pipette, add 1000 µL of primary stock into a pre-rinsed 10 mL volumetric flask and bring to volume with tridecane to prepare the 100 ng/mL (200 ng/mL OCDD-$^{13}C_{12}$) solution. Alternately, combine the purchased Wellington stock solutions (1 mL each) and bring to 10 mL with tridecane to prepare the 100 ng/mL (200 ng/mL OCDD-$^{13}C_{12}$) solution.

10.6.3. Sonicate for five minutes and transfer into clean labeled vials. Identification must include: ID#, log #, vial numbers, preparation date and preparer's initials.

10.6.4. Note: Identification - # denotes the next sequential number assigned tothe standard from the HRMS Standard Preparation Logbook.

10.6.5. Seal with Teflon tape and store in the standards refrigerator at <6°C.

10.6.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.6.7. This solution may otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent.

10.6.8. Prior to extraction, 20 µL of this solution is added to each sample.

10.7. Preparation of Primary Native Standard Spiking Solution

Compound	Concentration (µg/mL)
2,3,7,8-TCDF	0.40
2,3,7,8-TCDD	0.40
1,2,3,7,8-PeCDD	2.0
1,2,3,7,8-PeCDF	2.0
2,3,4,7,8-PeCDF	2.0
1,2,3,4,7,8-HxCDD	2.0
1,2,3,6,7,8-HxCDD	2.0
1,2,3,7,8,9-HxCDD	2.0
1,2,3,4,7,8-HxCDF	2.0
1,2,3,6,7,8-HxCDF	2.0
1,2,3,7,8,9-HxCDF	2.0
2,3,4,6,7,8-HxCDF	2.0
1,2,3,4,6,7,8-HpCDD	2.0
1,2,3,4,6,7,8-HpCDF	2.0
1,2,3,4,7,8,9-HpCDF	2.0
OCDF	4.0
OCDD	4.0

10.7.1. This is a purchased solution in nonane (Wellington, or equivalent).

NOTE: One vendor source and standards prepared from the source are used for the ICAL. The other vendor source and standards diluted from it are used as an independent validation of all standards purchased.

10.7.2. The native stock standard comes in a vial with approximately 1.2 mL present. After an ampule is cracked open, put the remaining volume in a crimp top amber vial.

10.7.3. NOTE: Identification - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.7.4. Store in standards refrigerator at <6°C.

10.7.5. Record all standard preparation information in Dioxin Stock Standard Preparation Logbook.

10.8. Preparation of Native Spiking Solution

10.8.1. Allow it to reach room temperature before using. Vortex for ~10 seconds before taking an aliquot.

10.8.2. Add 0.275 mL of native stock standard to a pre-rinsed 10 mL volumetric flask and bring to volume with tridecane to prepare this 10-100 ng/mL solution..

10.8.3. Vortex for ~30 seconds to ensure homogenization and transfer into 2 dram vials. Identification must include: Native Spiking Solution ID# ,log #, preparation date, expiration date and preparer's initials.

10.8.4. Note: Identification FS-N-# full scan native - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.8.5. Store in the standards refrigerator at <6°C until ready to use.

10.8.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.9. Preparation of Cleanup Standard Primary Stock

Compound	If Conc. is µg/mL	Amt. Added (µL)	Final Conc. (µg/mL)
$^{37}Cl_4$ 2,3,7,8-TCDD	50	200	1.0

10.9.1. The 50 µg/mL solution is purchased in nonane (Cambridge or equivalent). Vortex the vial, allow the solution to reach room temperature and add 200 µL of the solution to a pre-rinsed 10 mL volumetric flask. Bring to volume with tridecane to prepare this 1 µg/mL solution.

10.9.2. Transfer the Cleanup stock standard to a 2 dram vial with color coded tape. Identification must include: $^{37}Cl_4$ Cleanup Standard: Primary Stock ID# log #, preparation date, expiration date and preparer's initials.

10.9.3. NOTE: Identification - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.9.4. Seal vials with Teflon tape and store in the standards refrigerator at <6°C.

10.9.5. Record all standards preparation information in HRMS Standard Preparation Logbook.

10.10. Preparation of $^{37}Cl_4$ Cleanup Standard Secondary Stock

10.10.1. Vortex the standard and allow it to reach room temperature.

10.10.2. Using an Eppendorf pipette, add 1 mL of cleanup stock standard into a pre-rinsed 25 mL volumetric flask. Bring to volume with tridecane to prepare this 40 ng/mL solution.

10.10.3. Vortex for ~ 30 seconds, transfer to 2 dram vials. Identification must include: ID# (BCl4-#), log #, vial numbers, preparation date, expiration date and preparer's initials.

10.10.4. NOTE: Identification - # denotes the next sequential number assigned to BCl4 standard from the HRMS Standard Preparation Logbook.

10.10.5. Store in standards refrigerator at <6°C.

10.10.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.11. Preparation of $^{37}Cl_4$ Cleanup Standard Spiking Solution

10.11.1. Vortex and allow it to reach room temperature.

10.11.2. Using an Eppendorf pipette, add 2 mL of $^{37}Cl_4$ Cleanup stock standard into a pre-rinsed 100 mL volumetric flask and bring to volume with toluene to prepare this 800 pg/mL.

10.11.3. Sonicate for five minutes and transfer to pre-rinsed 6 dram vials. Identification must include ID# , log #, vial number, preparation date, expiration date and preparer's initials.

10.11.4. NOTE: Identification - # denotes the next sequential number assigned to thestandard from the HRMS Standard Preparation Logbook.

10.11.5. Vortex and store in standards refrigerator at <6°C.

10.11.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.11.7. 250 µL of this solution is added to each sample between extraction and enrichment.

10.12. Preparation of $^{13}C_{12}$ Recovery Standard Primary Stock

Compound	Conc. (µg/mL)
1,2,3,4-TCDD-$^{13}C_{12}$	2.0

1,2,3,7,8,9-HxCDD-$^{13}C_{12}$ 2.0

10.12.1. This solution is purchased at a concentration of 2.0 µg/mL from CIL or Wellington.

10.13. Preparation of $^{13}C_{12}$ Recovery Standard Spiking Solution

10.13.1. Sonicate the $^{13}C_{12}$ Primary Recovery Standard for five minutes and allow it to reach room temperature before using.

10.13.2. Using an Eppendorf pipette, add 1 mL of $^{13}C_{12}$ Recovery stock standard into a pre-rinsed 10 mL volumetric flask. Bring to volume with tridecane to prepare this 200 ng/mL solution.

10.13.3. Vortex, transfer to 2-dram vials labeled with tape. Identification must include: ID# , log #, vial numbers, preparation date, expiration date and preparer's initials.

10.13.4. Note: Identification - # denotes the next sequential number assigned tothe standard from the HRMS Standard Preparation Logbook.

10.13.5. Store in standards refrigerator at <6°C.

10.13.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.13.7. 10 µL of this solution is added to each sample during the final concentration of the extract.

10.13.8. This solution may otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent.

10.14. Initial Calibration Solutions

10.14.1. These solutions are purchased from CIL or Wellington.

PCDD/PCDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,7,8,9-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100

$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

10.14.2. The CS-3 is also available with the window defining and column resolution isomers in the same solution (See Quality Control Section).

10.14.3. Perfluorokersosene is used as the tuning and lock mass generating solution during the course of the analysis.

11. Calibration and Standardization

11.1. Table 11.1 – Calibration and Standardization

Calibration Metric	Parameter/Frequency	Criteria	Comments
Initial Calibration (ICAL)	Following proper tuning and documentation (see section 14,) prior to analyzing samples, the instrument is calibrated by analyzing a series of five standard solutions, one of which is at or below the reporting limit. The ICAL is performed when the continuing calibration solution is replaced by one from a different lot or when the continuing calibration does not pass the method specified criteria. Initial calibrations are generated using standard solutions containing target native and labeled PCDD/PCDF compounds. Response factors are calculated and averaged for each compound. These averages are used for quantification and for comparison to the daily continuing calibration.	A signal to noise ratio of >10:1 is required for each isomer. Ratios must be within 15% of theoretical values. Any outliners are flagged in Avalon. Initial calibration relative standard deviations must be less than 20% for the native and labeled isomers. (35% for labeled analytes in 1613B and DLM2.0) See 11.1.1.-11.1.3.	Additional standards are analyzed to demonstrate chromatographic resolution and stability of the ICAL. These consist of the continuing calibration solution described above, and a purchased solution (Wellington 5TDWD or equivalent) containing the isomers required to demonstrate the chromatographic resolution of the 2,3,7,8-TCDD (25% valley) and the presence of the first and last eluting isomers of each congener class. A solution (Wellington EPA-1613-CS3WT) is available and incorporates all of the above components into a single solution. Typically, samples are not analyzed until the above criteria can be met. In the event that samples are analyzed using an unacceptable curve, the samples must be re-analyzed with an acceptable initial calibration. If this is not possible, data must be qualified accordingly.
Initial Calibration	The initial calibration	±10% of Continuing	Sample analysis must not proceed without

Verification (ICV)	must be verified by analyzing a standard that is from a secondary vendor than the ICAL standards.	calibration range. See 11.1.1.-11.1.3.	successful second source verification.
Continuing Calibration Verification (CCV)	At the beginning and end of each 12-hour shift on days when initial calibrations are not performed. The ending CCAL is not required for Method 1613B.	For 8290/8290A - must yield response factors within ±20% (natives) to 30% (labeled) of the initial calibration. An additional 5% is allowed for the ending CCAL, with appropriate flags. See 11.1.1.-11.1.3. For DLM2.0, the ranges for both the beginning and ending calibrations are within ±20% (natives) to 35% (labeled) of the initial calibration. For Method 1613B, the statistical ranges are described in Attachment V.	Calibration must be verified prior to sample analysis. If the criteria are not met, the samples may be evaluated to determine the impact to the data results and preliminary results may be issued. If the samples appear to be the cause of an ending calibration verification failure, the results may be reported with appropriate flags, or, if sample remains, re-extraction may be performed to confirm the results.
Internal Standard	Internal standards are spiked into each sample prior to extraction in order to monitor the level of recovery that is achieved for each individual sample.	For methods 8290/8290A - acceptable recoveries range from 40 to 135% for the internal standards unless a deviation is due to variation in instrument response as a result of analytical interferences. The acceptance ranges for Method 1613B and DLM2.0 are described in Attachment V.	If used, results outside the target range must be flagged. The analysis may be repeated based on project requirements. See section 11.1.4.

11.1.1. Percent valley between 2,3,7,8-TCDD and any other peak in the column performance check must be <25%, relative to the height of 2,3,7,8-TCDD prior to the analysis of sample extracts. For DLM2.0 an acceptable column performance mix is also required at the end of each analytical sequence.

11.1.2. All peaks for a given PCDD/PCDF level of chlorination must elute within the window(s) set up for that particular class (determined from the window defining mix that contains first and last eluting isomers).

11.1.3. Native compounds must elute within ±2 seconds of the expected elution time relative to the elution times of the corresponding internal standards.

11.1.4. Internal Standards

11.1.4.1. Since the method is based on isotope dilution, the accuracy of native congener determinations is generally not affected when an internal standard recovery falls outside the target range. In general, samples will be considered acceptable with up to three internal

standards outside of the target range provided the signal to noise ratio of those standards is greater than or equal to 10:1. If more than 3 recoveries exceed established limits, the data may still be acceptable, but the analyst must use his/her discretion as to how to proceed. Any accepted exceedance must be narrated. If the failures are readily attributable to the analysis (not the extraction), the extract is re-analyzed.

Note: For Ohio VAP, samples with failing internal standards must be re-analyzed to confirm failures. Re-extraction may be necessary if failures are repeated.

Note: For South Carolina, samples with failing internal standards must be re-analyzed to confirm failures. Re-extraction may be necessary if failures are repeated. All failures must be flagged in the data reports.

11.1.4.2. If recoveries are outside of the target range and it appears that matrix interferences are the cause, samples can be diluted or processed through further clean-up steps and re-analyzed. If recoveries are still outside of the target ranges, the data are reported with flags or the samples are re-extracted.

11.1.5. Prior to each analytical sequence, the resolution of the mass spectrometer is verified to be 10,000 or greater. Hardcopies of the reference peaks are printed at the beginning and end of each analytical shift where possible.

11.1.6. The resolving power of the DB-5MS chromatographic column is checked daily using a standard solution containing 2,3,7,8-TCDD and the adjacent TCDD isomers. When second column confirmations are performed, the DB-225 (or equivalent) column resolution is checked using a standard solution containing 2,3,7,8-TCDF and the adjacent TCDF isomers. Acceptable performance is achieved when 2,3,7,8-TCDD or 2,3,7,8-TCDF is resolved from the adjacent isomers by a valley of 25% or less.

11.1.6.1. WIDNR require all positive detections to be confirmed by using the process defined in 11.1.6.

11.1.7. The group times for the selected-ion-monitoring data acquisitions are also checked daily by analyzing the column performance mix that contains the first and last eluting isomers of each congener class. In this way one is assured of collecting data representative of the total PCDD/PCDF content and the 2,3,7,8-substituted isomers are suitably resolved. The isomers described above are also available as part of the CS-3 calibration solution (EPA 1613 CS3 WT).

12. Procedure

12.1. Glassware Cleaning – See SOP S-MN-O-465 for full details on cleaning options

12.1.1. Wash and Kiln

12.1.1.1. Hand wash all glassware with Liquinox soap and water solution per the manufacturers suggestion

12.1.1.2. Rinse with regular water minimum of three times to remove soap

12.1.1.3. Rinse with DI water three times.

12.1.1.4. Bake at 500 C for minimum 3 hours.

12.1.2. Chemsolve Washing – optional cleaning

12.1.2.1. Wash with soap and water (water rinse). Soak in Chemsolve (or equivalent) for one hour (water rinse). NOTE: Chemsolve is typically changed every two weeks, at minimum, or after washing of samples found to contain very high analyte levels.

12.1.2.2. Rinse with tap water.

12.1.2.3. Rinse with 1 normal nitric acid and then a de-ionized water rinse

12.1.2.4. Rinse with acetone.

12.1.2.5. Air Dry.

12.1.2.6. Rinse with hexane and the solvent to be used for extraction just prior to glassware use.

12.1.3. Microwave extraction cells receive a modified cleaning. The cells are washed with soap and water, rinsed with 1:1 nitric acid, and rinsed with water and acetone.

12.1.4. Water Glassware Pre-extraction

12.1.4.1. Rinse all the separatory funnels three times with MeCl. Add ~60 mL MeCl to each separatory funnel, cap and rotate on the tumbler for two minutes for each rotation. Vent each rotation to release the pressure.

12.1.4.2. Drain the rinse solvent into each round bottom receiving vessel, swirl to rinse the inside of each vessel.

12.1.4.3. All round bottoms and concentration glassware will have been rinsed with MeCl during the cleaning cycles and be ready for use.

12.1.5. Microwave Cell Pre-extraction

12.1.5.1. Pre-rinse the cell with acetone and twice with hexane

12.1.5.2. Place 50 mL of Acetone:toluene 10:90 in the clean MARS cell (a disposable glass liner may be used to expidite cleaning of the cell- however solvent should be reduced by 10mls if liner is used.)

12.1.5.3. Blank the system with the same solvent to be used for extraction using the "Blank" program for extraction.

12.1.6. Soxhlet/Dean Stark Glassware Pre-extraction

12.1.6.1. Place 300 mL of toluene in the extractor along with approximately 5-8 Teflon boiling chips into the boiling flask.

12.1.6.2. Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1-2 drops of toluene per second must fall from the condenser tip into the receiver. Extract the apparatus for 3 hours.

12.1.6.3. After pre-extraction, disassemble the apparatus. Refill the apparatus with 200-250 mL fresh extraction solvent.

12.2. Preparation Prior to Sample Extraction

12.2.1. Aqueous samples containing one percent solids (or less) are extracted in separatory funnels.

12.2.1.1 Visually inspect each sample by holding up and looking through the glass container, if there is no visible sediment in the sample, treat the samples as it is <1% solid. If there is greater than 0.5 cm sediment present, determine the percent solids.

12.2.1.2 If upon pouring the sample in the separatory funnel, the sample is thick, viscous, or has notable suspended solids present, determine the percent solids before proceeding further.

12.2.2. In samples expected or known to contain high levels of the PCDDs and /or PCDFs, the smallest sample size representative of the entire sample should be used, and the extract diluted, if necessary.

12.2.3. Determination of Percent Solids

12.2.3.1. Weigh 5-10 grams (g) of sample to three significant figures into a tared weighing vessel.

12.2.3.2. Dry overnight (minimum of 12 hours) at 110 ± 5°C and cool in a desiccator. Reweigh.

12.2.3.3. % Solids = $\frac{\text{Wt dried sample (g)} \times 100}{\text{Wt wet sample (g)}}$

12.2.3.4. Data are recorded electronically and printed out as needed.

12.2.4. Grinding, Homogenization, and Blending

12.2.4.1. Prior to spiking, samples with particle size greater than 1 mm are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix dependent.

12.2.4.2. In general, hard particles can be reduced by grinding with a metal bar. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or by blending.

12.2.4.3. The grinding, homogenization, or blending procedures must be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

12.2.4.4. Tissue samples, certain papers and pulps, slurries and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. This process is often carried out at our Pace Analytical Services Green Bay laboratory.

12.3. Aqueous Samples- less than 0.5cm settled at the bottom of the jar (<1% Solids)

12.3.1. Preparation

12.3.1.1. Weigh the sample in the bottle to ± 1 g on a top loading balance. Record this weight.

12.3.1.2. Use appropriate indicator paper to verify the presence of residual chlorine and pH< 9. If there is residual chlorine is present treat with 80 mg Sodium Thiosulfate. If the pH is >9 add sufficient volume of sulfuric acid to get the pH between 7-9. Record the information on the extraction logs.

12.3.1.3. Spike 20 µL of the internal standard spiking into the bottle. Cap the bottle and mix by carefully shaking for 2 minutes. Allow equilibration for 1 hour.

12.3.1.4. For each batch set up QC according to section 13 by placing 1.0 L aliquots of reagent water in clean 1 L 1L Amber bottle. Spike as described in section 13.1. Allow equilibration for 1 hour with the samples.

12.3.1.5. Samples with >1% solids (more than 0.5cm settled at bottom of jar) are processed as described in section 12.5 However, the results are reported based on the total sample weight extracted and are considered as a water matrix.

12.3.2. Sample Extraction by Microsteam Distillation (2L) (not to be used for Ohio VAP)

12.3.2.1. Add 5mls of DI water to the microsteam concentrator, followed by 5mls of Iso-Octane. Place 3-5 glass beads into the top of the concentrator. These will fall halfway and be stopped by the catch barbs inside.

12.3.2.2. At the vent of the concentrator, place a plug of glass wool.

12.3.2.3. Place raw sample into 2L round bottom. Using silicate boiling stones, heat until rolling boil and reduce the power to 60% to hold boil without overheating the apparatus.

12.3.2.4. Once sample is boiling, extract for 3 hours and then turn of the mantle and allow everything to cool for at least 30 minutes.

12.3.2.5. Drain the extraction solvent and water remaining in the concentrator into a 60ml vial. Rinse the apparatus three times with Iso-ocatane (approximately 5 mls each), collecting the rinsates into the 60ml vial each time. Try to cover the entire inside of the apparatus. Remove and allow to cool for 5 minutes.

12.3.2.6. Decant the water using a small glass pipette, leaving behind the entire amount of Iso-Octane, and proceed with sample cleanup (12.12).

Note: Microsteam distillation is not approved for South Carolina. A separatory funnel method must be used in place of this method..

12.3.3. Sample Extraction by Separatory Funnel

Note: Aqueous samples originating in North and South Carolina must be extracted using separatory funnel extraction.

12.3.3.1. Quantitatively transfer sample into a separatory funnel with three 35 mL rinses of $MeCl_2$. Weight empty container for use in the determination of the amount of sample extracted.

12.3.3.2. Extract by shaking the separatory funnel, venting any backpressure for a minimum of 2 minutes.

12.3.3.3. If an emulsion layer forms, allow it to dissipate, or use mechanical such as centrifuge or chemical (salt,, ethanol etc.) means to break the emulsion. Once the emulsion is broken, continue the extraction.

12.3.3.4. After the extraction allow the layers to separate.

12.3.3.5. Remove the methylene chloride layer. Repeat the extraction two times with fresh aliquots of 100 mL of methylene chloride, combining the three solvent portions.

12.3.3.6. Transfer the methylene chloride through a 10 cm plug of sodium sulfate prebaked at 400 °C for 4 hours and glass wool to 500ml boiling flask. Assemble the round bottom flask and Snyder column. Add 30-50 mL Toluene through the Snyder column. Concentrate to approximately 10 mL using heating mantle.

12.3.3.7. Remove and allow to cool for 5 minutes.

12.3.3.8. Rinse Snyder column down into the flask with three 2 mL portions of hexane and proceed with sample cleanup (12.12).

12.4. Solid Phase Extraction (SPE)

12.4.1. Assemble the Solid Phase Extraction apparatus as follows:

12.4.1.1. Center an unused 47 mm Octadecyl (C18) extraction disk onto the metal screen on top of the port.

12.4.1.2. Center a 47 mm fiberglass filter paper directly over the extraction disk.

12.4.1.3. Place the glass funnel on top and secure with screw thread clamp. Ensure that the pump and SPE unit are connected to the solvent waste collection satellite at this point. Turn on the vacuum pump.

12.4.2. Rinse the disk by adding approximately 30 mL of methylene chloride.

12.4.3. Turn the valve so that it is open to the filtration apparatus and allow the methylene chloride to thoroughly saturate the disk. Do not let the disk go dry.

12.4.4. Open the valve(s) by moving the port handles to the waste position and allow half the methylene chloride to pass through. Once approximately half has passed through close the valve(s) by moving it back to its center position.

12.4.5. Open the valve to allow the remainder of the methylene chloride to be pulled through the disk. Close the valve when the disk appears dry.

12.4.6. Next add approximately 50 mL methanol to the funnel.

12.4.7. Again pull the methanol into the disk by vacuum and allow to sit for one to two minutes.

12.4.8. Turn the vacuum on again to pull most of the methanol through the disk. Do not allow the disk to go dry. Leave a small layer of methanol on top of the disk. If the disk does go dry, repeat the methylene chloride conditioning step 12.4.3.

12.4.9. Displace the methanol by rinsing the disk with one 50 mL aliquot of distilled water. Dump the methanol portion into a flammable waste container. Allow the water to penetrate the disk and let stand for one to two minutes. Then pull the remainder through the disk being careful to leave a layer of water on top. If the disk goes dry at this stage, repeat the previous steps beginning with the methylene chloride conditioning step 12.4.3.

12.4.10. Switch the tubing to the pump and SPE unit so that the unit is now connected to the water waste satellite. To extract the sample, carefully invert the sample container so that it rests on top of the funnel and allow the water to be pulled through the disk at the approximate rate of 100 mL per minute. If the sample is received in a wide mouth bottle, carefully pour approximately 200 mL at a time without letting the disks go dry.

12.4.11. Remove the sample container and allow the disk to remain under vacuum for approximately 30 seconds.

12.4.12. Screw on appropriate labeled 40ml vials to each port.

12.4.13. Rinse the sample container with 2 – 3 mL (1 large pipette worth) acetone and then pour onto the disk.

12.4.14. Open the valve(s) by moving the port valve handle(s) to the elute position and allow all the acetone to pass through the disk into the collection vial.

12.4.15. Rinse the bottle with 10 mL methylene chloride and pour onto the disk.

12.4.16. Open the valve(s) by moving the port valve handle(s) to the elute position so that approximately half the methylene chloride passes through the disk and into the collection vial and then let stand for 1.5-2 minutes.

12.4.17. Pull the remainder of the methylene chloride through the disk and collect into the collection vial.

12.4.18. Repeat steps 12.4.15-12.4.17, allowing the disk to stand under solution for no less than 1½ – 2 minutes each time.

12.4.19. Remove the 60 mL vials from the ports and empty the waste satellites appropriately. If no solvents have passed into the water waste satellites the water waste may be dumped down the drain.

12.4.20. Rinse the filtration apparatus with aliquots of toluene and acetone, respectively. For additional cleaning, the funnel may be washed with soap and water and then rinsed with acetone, toluene, and acetone aliquots, respectively.

12.4.21. Pipette the water layer off the top of each SPE sample extract.

12.4.22. Concentrate the SPE sample extract to approximately 1 mL on the nitrogen blow down units.

12.4.23. Concentrate the sample to almost dryness on the blow down unit and add 1 – 2 mL of hexane to complete the solvent exchange.

12.4.24. If the sample does go dry on the N-evap, then place the sample in a sonicator for 15 minutes and vortex to ensure that the analytes are in solution.

12.4.25. Add the appropriate amount of cleanup standard to the sample extract as with Separatory funnel, and proceed to cleanup.

Note: For South Carolina SPE, this method is not approved.

12.5. Aqueous Samples containing >1% Solids (more than 0.5cm of settled sediment at the bottom of the sample jar)

12.5.1. Preparation

12.5.1.1. Review the percent solids information to determine the sample size sufficient to provide 10 g equivalent dry weigh sample. Weigh a well mixed aliquot of each into a clean beaker, pre-extracted thimble or glass jar. In certain cases, i.e., sludge or waste matrices, this amount may be modified to a smaller aliquot to provide more workable extracts.

12.5.1.2. The sample may be separated using a centrifuge, and the liquid fraction decanted. With this procedure, the correct sample amount is first transferred into a different container for centrifuging. After centrifuging, the entire solid portion is mixed with sodium sulfate and transferred into a Soxhlet extraction thimble. If centrifuged, rinse any particulate off the sides of the secondary sample container with small quantities of methylene chloride.

12.5.1.3. Save aqueous phase. Measure the volume of the water, if greater than 100 mL of water is present, extract it in a separatory funnel or by SPE and combine with the solid extract, otherwise discard aqueous phase)

12.5.1.4. Spike with 20 µL of the internal standard spiking solution. Allow the sample to stand for 1 hour after spiking prior to moving on with extraction.

12.5.1.5. For each batch set up quality control (QC) according to section 13.1 by weighing 10g aliquots of clean sand into clean beakers or glass jars. Spike as described in 13.1. Allow the QC to stand for 1 hour after spiking prior to moving on with extraction.

12.5.1.6.

12.5.1.7. Extract the sample:

12.5.1.7.1. Fill the soxhlet with toluene to the neck of the soxhlet, allow it to drain into th round bottom flask. Turn on the mantle and reflux for 16-24 hours. Check the apparatus for foaming frequently during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.5.1.7.2. If applicable, drain the water from the receiver at 1-2 hours and 8-9 hours, or sooner if the receiver fills with water. Continue to reflux the sample for the 16-24 hours. Cool and disassemble the apparatus.

12.5.1.8. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration.

12.5.1.9. Concentrate to approximately 5-10 mL. Remove and allow to come to room temperature (approximately 5 minutes).

12.5.1.10. Rinse Snyder column down into the flask with ~5 mL portions of hexane.

12.5.1.11. If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes (12.12), combine with the filtrate in a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup (12.12).

12.6. Soil/Solid by Microwave Assisted Extraction

Note: Solid samples originating in South Carolina must be extracted using Soxhlet extraction. Do not use MAE for South Carolina samples.

12.6.1. Blank extract the MAE vessels with 90:10 Toluene:Acetone

12.6.2. Weigh a 10-gram aliquot (dry weight) of the homogenized sample and place into a microwave extraction cell. If the sample material is wet, it may be dried with the addition of hydromatrix after the sample has been weighed.

12.6.3. Spike the sample with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour prior to proceeding with extraction.

12.6.4. For each batch, set up QC according to section 13.1 by weighing 10g aliquots of clean sand into clean microwave cells. Spike as described in 13.1. Allow the QC to stand for 1 hour prior to proceeding with extraction.

12.6.5. Add 50 mL of Acetone:toluene 10:90 to the extraction cell, insert the Teflon plug and the cap. Seal the screw on cap tightly.

12.6.6. Insert the cells into the microwave and run using the "1613" program. The program is as follows:

Power				
Max	**%**	**Ramp**	**Degrees C**	**Hold Time (min)**
800w	80	10:00	125	20
1600w	100	10:00	150	50

12.6.7. After extraction program is complete (approximately 2 hours) sonicate the cells for a minimum of 20 minutes.

12.6.8. Carefully open each cell containing the extracted sample and collect the solvent extract.

12.6.9. Rinse the cell and sample material twice with 10 mL of hexane, combining the hexane with the original solvent extract.

12.6.10. The Acetone must be removed from the extract prior to cleanup.

12.6.11. The solvent layer is ready for silica column cleanup (12.12)

12.7. Soil/Solid Samples by Soxhlet

12.7.1. Preparation

12.7.1.1. Weigh a 10-gram aliquot (dry weight) of the homogenized sample, and place into a Soxhlet thimble. If the "solid" sample contains >90% moisture, treat like the waters >1% solids in 12.5. If the sample material is wet, but less than 90% moisture, dry it by mixing with extracted anhydrous sodium sulfate before adding to the Soxhlet thimble. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene,) no sodium sulfate should be added.

12.7.1.2. Spike the sample aliquot with 20 µL internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding to extraction.

12.7.1.3. For each batch set up QC according to 13.1 by weighing 10g aliquots of clean sand into clean Soxhlet thimbles or clean beakers. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding to extraction.

12.7.2. Sample Extraction

12.7.2.1. Place the prepared sample in the thimble into the Soxhlet extractor. The Dean-Stark attachments maybe utilized in place of the sodium sulfate drying step.

12.7.2.2. Add 300 mL of toluene and reflux for a minimum of 16 hours. Cycle at a rate of three cycles per hour. If applicable, drain the water from the receiver as needed.

12.7.2.3. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

12.7.2.4. Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

12.7.2.5. Rinse Snyder column down into the flask with three 2 mL portions of hexane.

12.7.2.6. If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes (12.12), transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup (12.12).

12.8. Preparation and Extraction of Fly Ash Samples

12.8.1. Weigh a 10g aliquot of the homogenized sample and an equivalent amount of anhydrous sodium sulfate into a clean beaker. Mix well. NOTE: If high levels are expected, a smaller (1 gram) aliquot may be extracted. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene,) no sodium sulfate should be added.

12.8.2. Spike the sample aliquot with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding with extraction.

12.8.3. For each batch set up QC according to 13.1 by weighing 10g aliquots of clean sand into clean Soxhlet thimbles or clean beakers. Spike as described in 13.1. Allow QC to stand for 1 hour before proceeding with extraction.

12.8.4. Place each prepared fly ash sample into a thimble and place in the Soxhlet apparatus.

12.8.5. Add 300 mL toluene and extract for 16 hours, maintaining three cycles per hour.

12.8.6. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

12.8.7. Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

12.8.8. Rinse Snyder column down into the flask with ~5 mL portions of hexane.

12.8.9. If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes (12.12), transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup (12.12).

12.9. Milk and Milk Product Samples

12.9.1. Accurately measure a 100 mL aliquot of milk and transfer to a 2 liter separatory funnel.

12.9.2. Spike the sample aliquot with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding with extraction.

12.9.3. For each batch set up QC according to 13.1 by 100 mL aliquots of de-ionized water into clean separatory funnels. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding with extraction

12.9.4. Add 300 mL of 1.5M potassium oxalate solution and 600 mL of de-ionized water to each sample in the separatory funnel.

12.9.5. Gently shake the separatory funnel for 8-10 minutes.

12.9.6. Add 150 mL of 1:1:1 ethanol/ether/hexane to the sample and shake gently for 3-4 minutes.

12.9.7. Allow the layers to separate 15-20 minutes.

12.9.8. Collect the milk (bottom layer) and emulsion layers in a clean 2 L beaker. (The emulsion layer can be reduced by adding small volumes (10-30 mL) of the 1:1:1 solvent mixture to the separatory funnel after separation of the layers).

12.9.9. Transfer the clear organic layer directly to a Kuderna-Danish concentrator and set aside.

12.9.10. Transfer the milk and emulsion back to the separatory funnel and repeat the extraction two more times. Combine the organic layers to the K-D flask and save the emulsion layer in a 500 mL separatory funnel.

12.9.11. After the final extraction, rinse the 2 L separatory funnel with 60 mL of the 1:1:1 solvent mixture and add to the K-D flask.

12.9.12. Concentrate the extract to 2 mL and allow cooling.

12.9.13. Quantitatively transfer the extract into the separatory funnel containing the emulsion and add 80 mL hexane.

12.9.14. Perform the acid washes and cleanup (12.12) as described. For milk samples, acid cleanup is not considered optional.

NOTE: The first acid wash should not be shaken. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow separation for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

12.10. Preparation of Tissue Samples (Environmental)

12.10.1. If the sample is supplied as whole fish or fillets, grind the sample using a meat grinder or blender.

12.10.2. Weigh a 10 (use 20 grams if EU requirements apply) gram aliquot of the homogenized sample into a clean beaker. Mix in enough extracted anhydrous sodium sulfate to dry the sample (usually approximately twice the tissue weight. Quantitatively transfer the sample into a clean Soxhlet thimble and top with extracted glass wool.

12.10.3. Spike the sample aliquot with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding with extraction.

12.10.4. For each batch set up QC according to 13.1 by weighing 10 g aliquots of clean tuna or reference oil matrix and place each aliquot into a Soxhlet thimble. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding with extraction

12.10.5. Store any remaining sample in the freezer at approximately -18^{o}C.

12.10.6. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene,) no sodium sulfate should be added.

12.10.7. Place the loaded thimble into the Soxhlet apparatus.

12.10.8. Add 250 mL of hexane/methylene chloride (1:1 v/v) and reflux for a minimum of 18-hours.

12.10.9. Alternatively, the sample can be extracted using Soxhlet Dean-Stark apparatus and toluene. No sodium sulfate is used with this option.

12.10.10. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. Add 30-50 mL toluene through the Snyder column, allow it to drain into the round bottom flask.

12.10.11. Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

12.10.12. Rinse Snyder column down into the flask with three 2 mL portions of hexane.

12.10.13. Perform the acid washes and cleanup as described (12.12). For tissue and food samples, acid cleanup is not considered optional. The column acid wash procedure may be preferable to the separatory funnel procedure.

NOTE: The first acid wash should not be shaken. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow separation for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

12.10.14. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

12.10.15.

12.11. Preparation of Oil Based Food Product Samples

12.11.1. Canola oil or equivalentis used as the reference matrix for oil based food and feed matrices.

12.11.2. Weigh out a 10-gram aliquot (use 20 grams if EU requirements apply) of the oil based sample into a clean 8 ounce soil jar and spike the aliquot with the internal standard spiking solution.

12.11.3. Spike the other aliquot(s) with 20 µL of the internal standard spiking solution and with 10 µL of the native spiking solution (20 uL of a 2x dilution is also acceptable) This (they) serve(s) as the laboratory control spike(s). If matrix spikes are prepared with the extraction batch, only one laboratory spike is required. If included, matrix spikes are prepared in the same manner as laboratory spikes except using sample material rather than reference matrix..

12.11.4. For each batch set up QC according to 13.1 by weighing 10-gram aliquots of the canola oil reference matrix and place each aliquot into a clean beaker. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding with extraction

12.11.5. Spike one reference sample with 20 µL of the internal standard spiking solution. This aliquot serves as the method blank. Allow the samples to stand for 1 hour before proceeding with extraction.

12.11.6. Add 50 mL of hexane to the sample. Gently shake to mix the oil and solvent, allow the sample to sit for 1 hour to dissolve the oil into solution..

12.11.7. Proceed to"Super Carbon First" enrichment (12.12).

12.12. Extract Enrichment/Cleanup Procedures

12.12.1. Back Extraction with Acid – Micro scale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color. If the extract is cloudy, emulisive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e.

multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). Most samples undergo this procedure, including all QC samples in associated batch.

12.12.1.1. Spike each extract with 250 µL of the clean-up standard..

12.12.1.2. Quantitatively transfer H2O and soxhlet extracts with 15 mL of hexane to 40 mL vials.

12.12.1.3. Partition the extract against 2-3 mL concentrated sulfuric acid. Agitate the samples for two minutes with periodic venting into a hood. Remove and discard the acidic bottom layer. Emulsions may be broken down by mechanical or chemical means.

12.12.1.4. Repeat 12.12.1.3, the acid washing, until no color is visible in the aqueous layer, to a maximum of four washings.

12.12.1.5. Acid waste is collected, then stored in labeled containers for disposal. Use caution when handling.

12.12.1.6. Repeat step 12.12.1.3, but substitute buffer solution (100 mL 0.5 M KH2PO4).

12.12.1.7. Concentrate extract to approximately 1 mL on the N-evap and proceed with column cleanup. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS!

12.12.2. Back Extraction with Acid – Macro scale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color of the extract is cloudy, emulsive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). If samples undergo this procedure, all QC samples in associated batch must go through the same process at least once.

12.12.2.1. Spike the extract with 250 µL of the cleanup standard..

12.12.2.2. Quantitatively transfer concentrated extracts to an 8 oz flint glass jar with 50ml of N-Hexane.

12.12.2.3. Quantitatively transfer and partition the extract in 50 mL concentrated sulfuric acid. Agitate briefly with periodic venting into a hood. Remove and discard the aqueous bottom layer. Emulsions may be broken down by mechanical or chemical means.

12.12.2.4. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.12.2.5. Acid waste is collected and stored in labeled containers for disposal. Use caution when handling. Repeat step 12.12.2.3 but substitute DI water, as needed.

12.12.3. "Super Carbon First" Column

12.12.3.1. Bake the Carbon and Celite at 130^{o}C for 6 hours. .

12.12.3.2. Prepare carbon/Celite packing by mixing 18% (by weight) 100–400 mesh active carbon (Pre-extracted in Soxhlet with Toluene overnight) and 82% (by weight) Celite. Mix thoroughly. .

12.12.3.3. The column is prepared using 18mm tubing in one foot increments. These are designed to be used only once, and discarded after use.

12.12.3.4. Insert a silanized glass wool plug at one end (~2" from the end of the column) and pack with ~1/2 inch of Celite followed by 3.0 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug. Note: Tap the column between layers to level out the resins.

12.12.3.5. Rinse the column "clean (Celite)" side up with 30 mL of hexane. The flow rate must be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/min, discard the column. Discard the rinses.

12.12.3.6. While the column is still wet with hexane, quantitatively transfer the sample extract to the top of the column and rinse the jar with two 10 mL aliquots of hexane. If necessary use a 3rd 10 mL hexane rinse to completely transfer the sample to the column. Note: Add the sample and rinses slowly using sonication or vortexing as needed to keep the sample dissolved.

12.12.3.7. Collect the hexane containing the sample matrix as waste, periodically rinsing the bottom of the column with fresh hexane to remove any residual oil matrix from the column.

12.12.3.8. Eluet the column with 30 mL Methanol. Follow this elution with 10 mL Hexane, discard in waste collection.

12.12.3.9. Carefully turn the column upside down and elute the PCDDs and PCDFs with 60 mL of toluene.

12.12.3.10. Evaporate the toluene to near dryness, add 5-10 mL of hexane and spike the sample with 250 uL cleanup standard before proceeding to the silica column and alumina column cleanups described below.

12.12.4. Silica Column

12.12.4.1. Vertically clamp a disposable glass column, 15 mm ID x 35 cm. Rinse with hexane, air dry, and place a pre-extracted silanized glass wool plug into bottom.

12.12.4.2. Pack the column in the following order (bottom to top): 1 g neutral silica, 2 g basic silica, 4 g acidic silica, 2 g neutral silica and 2 g sodium sulfate. Between each layer, tap the column to settle the silica. Wet column with 15-20 mL hexane after all layers are added, allow this to drain into the alumina column in 12.12.5 if doing the stacked columns Plug the end of the column with a septum when it starts dripping. Check the column for channeling. If channeling is observed, discard the column. DO NOT allow the column to go dry.

12.12.4.3. Spike the extract with the cleanup standard, if it has not already been added in 12.12.3.10.

12.12.4.4. Quantitatively transfer the sample extract onto the column using two 2 mL rinses of hexane. Break off the tip of the column containing the septum. Elute until the solvent just covers the silica. Do NOT let the column go dry.

12.12.4.5. Elute the column with 80 mL hexane onto the alumina column in 12.12.5 if doing stacked columns.

12.12.4.6. Jumbo-silica columns are prepared using three times the amount of the silica noted above in each layer of the column. Larger macro-silica columns may be prepared using nine times the amount of the silica noted above in each layer of the column. These columns are prepared in drying tubes and are eluted with approximately 300 mL or 500 mL of hexane, respectively.

12.12.5. Alumina Column

12.12.5.1. Pack a silanized glass wool plug into the bottom of a disposable glass column (15 mm ID x 35 mm). Pack the column in the following order: 4 g of prebaked (400 °C for 4 hour) anhydrous sodium sulfate, 7 g of neutral alumina, and 4 g of anhydrous sodium sulfate to cover the alumina. Between layers, tap the top of the column gently to settle the adsorbents.

12.12.5.2. Elute with 15-20 mL hexane from 12.12.4.2. Discard the eluate. Check the column for channeling. If channeling is present, discard the column. DO NOT TAP A WETTED COLUMN AND DO NOT LET THE COLUMN GO DRY.

12.12.5.3. The 80 mLsample from 12.12.4.5 is eluted into the alumina column . Disassemble and dispose of the silica column then elute with 40 ml of 60% (v/v) methylene chloride in hexane. Collect this fraction in a 12 dram vial.

12.12.5.4. Concentrate the extract to near dryness using an N-evap apparatus.

12.12.5.5. Solids stack the alumina column on top of the below carbon column and continue the cleanup process.

12.12.6. Carbon Column

12.12.6.1. Bake the Carbon at 130°C for 6 hours.

12.12.6.2. Prepare carbon/Celite packing by mixing 18% (by weight) 100-400 mesh active carbon (pre-extracted in soxhlet with acetone overnight) and 82% (by weight) Celite. Mix thoroughly ..

12.12.6.3. Prepare a 15 mm glass tube about one foot in length.

12.12.6.4. Insert a silanized glass wool plug at one end and pack with 1 cm of Celite followed by ~1 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug.

12.12.6.5. Rinse the column "clean (Celite)" side up sequentially with 10-15 mL hexane. The flow rate must be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/minute, discard the column. Discard the rinses.

12.12.6.6. While the column is still wet with hexane, allow the samples elute from 12.12.5.3, dispose of the solvent and remove the alumina column.

12.12.6.7. Turn the column upside down and elute the PCDDs and PCDFs with 15 mL of toluene. Proceed to Final Extract Transfer.

12.13. Final Extract Preparation

12.13.1. Extract Transfer

12.13.1.1. Concentrate the extract under a gentle stream of nitrogen to a volume of less than 1 mL. Do NOT blow the sample so the portions of the solvent "ride" up the sides of the glass vial. The temperature of the N-Evap bath must be <42°C

12.13.1.2. Add 10 µL of tridecane using a calibrated Eppendorf pipette to an autosampler vial to act as a keeper solvent.

12.13.1.3. Quantitatively transfer the extract to the autosampler vial. Rinse the original vial with less than 1 mL of methylene chloride/hexane (60:40 V:V). Transfer rinsate to the autosampler vial. Repeat the rinse of the auto-sampler vial with two additional aliquots (<1 mL) of methylene chloride/hexane. Then blow down extract to the level of the 10 uL keeper solvent.

12.13.1.4. Add the 10 µL of recovery standard to the extract with a calibrated Eppendorf pipette for a final volume of 20 µL and cap. Vortex each of the sample vials.

12.13.1.5. Transfer the extracts to the analytical laboratory for analysis. Extracts must be stored in the dark at approximately -10°C.

13. Quality Control

13.1. Table 13.1 – Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Spike 20 µL of the internal standard spiking solution into one reference matrix. Note: When setting up method blanks, the glassware used must be varied randomly amongst the sets used for sample extraction.	One method blank is typically prepared with each twenty samples of any given matrix.	A method blank or solvent blank must be analyzed between standards and samples to demonstrate lack of PCDD/PCDF carryover. Method blanks are treated like samples in the analytical sequence. For DLM2.0 the method blank	If the method blank contains significant PCDDs/PCDFs, find and correct the source of the problem. If the contamination appears to be instrument related, correct the problem, analyze a solvent blank, and reanalyze the method blank before proceeding with samples. If the contamination appears to be from the extraction or enrichment steps, the analysis of samples may continue. If the sample shows similar contamination it must be re-extracted,

			associated with a given sample must be analyzed at the beginning of the same sequence as the sample. For Ohio VAP: < RL at a minimum	if possible. All associated sample results must be qualified for method blank contamination when any analyte is detected in the method blank at 10% or more of the sample concentration. If the method blank shows no contamination above the reporting level calibration solution, analysis of samples may continue. However, all associated sample results must be qualified for method blank contamination when any analyte is detected in the method blank at 10% of more of the sample concentration ***Exception:*** For Ohio VAP analyte must be re-extracted if >RL under any circumstances.) See Attachment VIII for special DLM2.0 method blank requirements.
Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD)	Spike 20 µL of internal standard spiking solution and 10 µL (or 20uL of 2x dilution) of the native spiking solution into the remaining reference matrix. Note: For Ohio VAP, LCSD is not analyzed,	At a minimum, one laboratory control spike is prepared with each batch of samples (up to 20) of any given matrix. For batches that DO NOT have sufficient sample volume to perform an MS/Sample duplicate or MS/MSD set, a laboratory control spike duplicate must be performed to show precision. NOTE: Only one laboratory control spike is required when an MS/Sample duplicate or MS/MSD set are prepared in the same batch.	For method 8290/8290A, control limits are set at 70-130%. The ranges for Method 1613B are provided in Attachment V. DLM2.0 also utilizes the 1613B ranges. If an LCSD was required, the RPD value must also be calculated.	Recoveries of up to 2 native analytes outside the acceptable range do not invalidate the data but provide information, which is used by the laboratory to monitor recovery trends and to assure optimization of the method. Any failure cannot occur for the same set of analytes in two consecutive batches. Affected samples must be re-extracted and reanalyzed if possible, or the data must be qualified with a detailed explanation of data impact in the narrative section of the final report. Accuracy of the standard spiking solutions must, at a minimum, be verified quarterly by comparison of the solutions to certified native materials obtained from a second source or batch. If the recoveries are not within the control limits, data must be evaluated to determine the impact on the associated samples. If it is determined that the instrument may be the cause of the outlier, the QC must be reanalyzed to confirm results as well as any associated samples that may have been impacted by the instrumentation failure. If it is determined that the cause is due to poor extraction, all associated samples must be re-extracted and reanalyzed or qualified accordingly.
Matrix Spike (MS)/ Matrix Spike Duplicate (MSD) or Matrix Spike (MS) /Sample Duplicate (DUP)	Place the appropriate amount of the client supplied duplicate sample into clean apparatus. Spike 20 µL of internal standard spiking solution and 10 µL of the native spiking solution (or 20uL of a 2x dilution)	One matrix spike/spike duplicate set must be prepared with the extracted sample batch (up to 20 samples) when sufficient	For Method 8290/8290A, the recovery limits of the native PCDD/PCDF analytes in the spiked samples range from 70 -130% and 20% RPD. For Method 1613B, use the laboratory spike	Recoveries of selected analytes outside the acceptable range do not invalidate the data but provide information, which is used by the laboratory to monitor recovery trends and to assure optimization of the method. This is particularly true of MS/MSD recoveries where native PCDD/PCDF are subject to the effects of the sample source. Data must be qualified accordingly on the final report.

	into the client-supplied duplicate samples (if supplied). If there is insufficient sample volume for MS/MSD or MS/Sample Duplicate see 13.1.1. Note: MS is optional for Ohio VAP.	sample volume is supplied. (If insufficient sample volume is available, refer to Section 13.1.1). Matrix spikes are not performed for DLM2.0 since approved results forms are not available.	(OPR) limits from attachment V.	If native recoveries in the MS/MSD indicate a laboratory method performance problem (i.e. >2 recoveries are outside the acceptance limits, but the original sample does not appear to be the cause), analysis of the associated batch samples must be suspect until corrective action is taken to determine the root cause of the problem, and the problem is negated. Accuracy of the standard spiking solutions must, at a minimum, be verified quarterly by comparison of the solutions to certified native materials obtained from a second source or batch. For Minnesota Admin Contract clients – all MS/MSD failures require reanalysis of the MS/MSD and the original sample. If it is still out of control, investigate and document the cause in the associated narrative as well as qualifying appropriately. For Ohio VAP samples, if the outlier is an analyte of interest and corrective actions do not result in acceptable data, the samples must be re-extracted. If re-extraction is not possible due to depleted sample volume, then contact the client for further instructions. The client may want to re-submit the sample or have the lab qualify the data and narrate as appropriate. Recoveries impacted by elevated sample levels (>2 times the spike level) are not required to be within the acceptance range.

13.1.1. For each batch (up to 20 samples) to be extracted in the same 12 hour shift, place two aliquots of the reference matrix into clean apparatus (See extraction sections for reference matrix type). One reference matrix must serve as the method blank and the other must be a laboratory control sample (LCS). Include one additional aliquot of reference matrix if insufficient sample volume to perform an MS/Sample duplicate or MS/MSD is found. This aliquot must serve as a laboratory control spike duplicate (LCSD) for the batch to show precision. Note: Only one lab control spike is required when an MS/Sample duplicate or MS/MSD set is prepared in the same batch.

13.2. Extraction Corrective Action (Does not apply for Ohio VAP)

13.2.1. If a laboratory error occurs during the extraction process that results in the loss of an extract prior to final concentration and transfer of the sample, a new aliquot may be re-extracted and added to the original batch. The new aliquot must be set up within 12 hours of the set up of the first sample in the extraction batch or it must be put into a new batch. This may include a QC aliquot.

13.2.2. Make note of any error and corrective action on the extraction sheet. Include times of laboratory error and re-set up of the aliquot.

13.3. Reporting and Review

13.3.1. Reports are generated using the Avalon software package. Reporting options are chosen to match the requirements for individual clients.

13.3.2. Units/Significant Figures

13.3.2.1. Values are reported to two significant figures. Aqueous samples are routinely reported in units of pg/L and solid matrices are reported in ng/kg. Other units are available upon request.

13.3.3. Data Qualifiers/Flags - The information typically reported is summarized below.

13.3.3.1. Base Report

13.3.3.1.1. Case Narrative including client name, address, project information, introduction, sample information, and discussion of results.

13.3.3.1.2. Copies of chain of custody documents and analytical requests

13.3.3.1.3. Sample Analysis Results

13.3.3.2. Full Report

13.3.3.2.1. Those items listed in base report summary

13.3.3.2.2. Raw data including sample, QC sample and standards

13.3.3.2.3. Selected ion current profiles (chromatograms)

13.3.3.2.4. Communications records

13.3.3.2.5. Extraction and login forms

13.3.3.2.6. Instrument resolution checks

13.3.3.2.7. Calibration Results

13.3.4. Levels of Review

13.3.4.1. Each sample work-up must be rechecked for work-up, header information and data entry accuracy. The results of this review are recorded on the raw data sheet.

13.3.4.2. All data generated during analysis are peer reviewed and a review checklist is completed. The project manager reviews the data prior to inclusion in the final report.

13.3.5. Data Archiving or Filing

13.3.5.1. All analytical results are stored in Avalon.

13.3.5.2. After reporting, the complete project file is archived in the permanent chemistry archive.

14. Data Analysis and Calculations

14.1. Sample Analysis

14.1.1. Introduce PFK into the batch inlet and tune the instrument to a resolution of ≥ 10,000 (M/ΔM, 10% valley) using a PFK peak within the analysis mass range (M/Z 331 or 381). Tuning is accomplished by adjusting the various instrument voltages displayed on the tune pages in the "AutoSpec" window to maximize both signal strength and resolution (peak width). If the scan width is set to 200 ppm, a peak crossing the 5% y axis at 50% of the displayed width will be considered 10,000 resolution. If peak shape and intensity appear reasonable, tuning may just be a matter of optimizing each of the variable lens voltages as fine tuning. If irregularities are present, consult with an experienced analyst. Print, sign and date a copy showing the reference peak resolution. This record is scanned into Avalon. Note: The instrument can be programmed to centroid and obtain static resolution printouts at any time during the course of the run. Using this ability, one may either obtain the first functional group in its entirety, or all functional groups. The choice is left to the operator, but may be client directed. As the system is inherently pre-disposed to hysteresis, it is critical that the "Cycle magnet through zero" radio box be checked on each individual function. If this is not done, it is likely that function one of the next run will be largely lost. Subsequent injections will not suffer any consequence however.

14.1.2. Typical Operating conditions include:

Trap current:	500 µA
Electron Energy:	32 ± 5 eV (40 ± 5 eV for Thermo instruments)
Source Temperature:	270 °C
Emission/Trap Ratio:	≤ 3

Accelerating Voltage: 8000 eV (5000 eV for Thermo instruments)

14.1.3. Once the tune objectives have been met, the Waters instruments need to complete a selected ion calibration to ensure proper operation. Open the "experiment calibration" window and ensure that "dioxfur" is selected as the experiment file. Next, start the calibration and check the box on the right hand side to center the reference peak. All reference peaks bracketing the quantitation masses need to be at least 10,000 resolution. Once the peak is centered, choose the "next" button. Repeat this centering and continuing process until all five mass groupings have been completed.

14.1.4. Once the mass calibration is complete, change to the "MassLynx" window and enter the analytical information (filename, sample ID, etc.) onto the table. The tables are saved according to an instrument date code. For example, table U130102A would be instrument "U" from year 2013, month 01 and day 02. The A signifies the first run sequence from that day. A second sequence would be U130101B. Sample filenames follow the same format and have a sequential number added to the end of the code. For example U130101A_01 would be the first injection from that sequence.

14.1.5. The first injection of the sequence is typically the calibration standard (that also contains the column resolution and window defining isomers). This is generally followed by laboratory spikes and matrix spikes if they are available. Next a blank (instrument or method) is run. Some type of blank must be analyzed between the calibration standard and non-spiked sample extracts. Method blanks are considered the same as sample extracts and may be analyzed either after spikes or with the sample extracts if an instrument blank was included in the sequence. The sample extracts are next followed by the ending calibration standard. Note: If the sequence is running at a time when staff are present, it is advantageous to check the calibration standards and blank promptly so corrective action can be taken if they do not meet the criteria in Table 11.1 and Table 13.1.

14.2. Qualitative Analysis

14.2.1. Samples are queued as discussed in the data processing section of this SOP. In order for a peak to be accepted as a PCDD/PCDF isomer, the following criteria must be met:

14.2.1.1. Intensity ratios must be within 15% of the theoretical value.

14.2.1.2. The signal to noise of the peak versus the background noise must be >2.5:1.

14.2.1.3. No PCDF peak may have a co-eluting peak in the mass window monitored for polychlorinated diphenylethers.

14.2.1.4. The peak elutes within the retention time determined from the analysis of the column performance window mix standard.

14.3. Data Processing

14.3.1. Data is collected using MassLynx Version 4.0 or Xcalibur Version 2.0 software. The software is run on personal computers running Microsoft Windows XP.

14.3.2. The raw data files are imported into the Avalon (Version 3.0) data processing program for integration. Information on how to use Avalon is available in the Avalon manual that can be accessed on the HRMS group computers. Also, since the DB-5MS capillary column gives partial resolution of 2,3,7,8-TCDF isomer (typically 30-40% valley or less), second column confirmation analyses are only performed if co-elution is exhibited or based upon project requirements. If 25% valley is achieved no further confirmation is required.

14.3.2.1. The confirmation is required for all samples exhibiting positive detections for 2,3,7,8-TCDF for samples from WIDNR.

14.3.3. Note that the window mixture does not need to be queued. Visually inspect the chromatographic data to ascertain the elution times of the first and last eluting isomers of each congener class and chromatographic resolution.

14.3.4. With the elution time information recorded, adjust the method file times so that the group changes occur at points between the elution time of the last isomer of a given class and the first

isomer of the following class. The first PeCDF isomer is monitored in Group 1 with the group change set approximately 30 seconds later.

14.4. Calculations

14.4.1. Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for each congener using Equation 1.

Equation 1

$$\%RSD = \frac{SD}{\overline{X}} x100$$

Where:
RSD = Relative standard deviation.
SD = Standard deviation of average RFs for a compound
$\overline{X}$ = Mean of 5 initial RFs for a congener

14.4.2. The standard deviation is calculated following Equation 2.

Equation 2

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_1 - \overline{RF}\right)^2}{n-1}}$$

Where:
RF_1 = Each individual response factor
$\overline{RF}$ = Mean of the Response Factor
n = The total number of values

14.4.3. Calculate the percent difference using Equation 3.

Equation 3

$$\%Difference = \frac{RF_1 - RF_c}{RF_1} x100$$

Where:
RF_1=Average response factor from initial calibration.
RF_c=Response factor from current verification check standard

14.4.4. The PCDD/PCDF isomers (native or labeled) are quantified by comparison of their responses to those of the corresponding/appropriate labeled standard. Relative response factors are calculated from analyses of standard mixtures containing representatives of each of the PCDD/PCDF congener classes at five concentration levels, and each of the internal and recovery standards at one concentration level. The PCDD/PCDF response factors are calculated by comparing the sum of the responses from the two ion masses monitored for each chlorine congener class to the sum of the responses from the two ion masses of the corresponding isotopically labeled standard. The formula for the response factor calculation is:

Equation 4

$$Rf = \frac{Aa \times Qs}{As \times Qa}$$

Where:

Rf = Response factor
Aa = Sum of integrated areas for analyte
Qs = Quantity of labeled standard
As = Sum of integrated areas for labeled standard
Qa = Quantity of analyte

14.4.5. The levels of PCDD/PCDF in the samples are quantified using the following equation:

Equation 5

$$C = \frac{An \times Qis}{Ais \times W \times Rf}$$

Where:
C = Concentration of target isomer or congener class
An = Sum of integrated areas for the target isomer or congener class
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard
W = Sample amount (dry weight for soil samples)
Rf = Response factor

14.4.6. The levels of interferences in samples are quantified using the following equation:

Equation 6

$$EMPC = \frac{An \times Qis}{Ais \times W \times Rf}$$

Where:
EMPC = Estimated Maximum Possible Concentration of target isomer
An = Sum of integrated areas for the target isomer (Note that the signal from the ion that yields the lowest concentration is used to calculate the secondary signal using the theoretical isotope ratio.)
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard
W = Sample amount (dry weight for soil samples)
Rf = Response factor

14.4.6.1. An Estimated Detection Limit (EDL), based on the signal to noise ratio of the noise level of the ion of interest versus the appropriate standard, is calculated for each sample and isomer. The equation used for calculating the EDL is:

Equation 7

$$EDL = \frac{Hn \times Qis \times 2.5}{His \times W \times Rf}$$

Where:
EDL = Estimated Detection Limit
Hn = Sum of noise heights for target isomer
Qis = Quantity of labeled internal standard added to the sample
His = Sum of signal heights from labeled internal standard
W = Initial sample weight or volume
Rf = Response factor

Note: If a signal is present which does not meet the ion ratio requirement but is greater than 2:5:1 S/N, the 2.5 factor is omitted for that ion mass.

14.4.7. A quantitation limit equal to the concentration of the lowest calibration standard is used for this method and is calculated as follows:

Equation 8

$$QL = \frac{C \times V}{W}$$

Where:
QL = Quantitation Limit
C = Concentration of lowest level standard
V = Volume of final extract
W = Initial sample weight (dry weight for soil samples) or volume

14.4.7.1. Isomers present below the QL are reported as not detected at the QL. If the calculated EDL is above the QL for any given isomer, the signal to noise based EDL is reported for that isomer. If requested by a client, the EDL values may be be reported for all analytes. Any positive values below the concentration of the lowest calibration standard must be flagged "J" as estimated values.

14.4.7.2. The recovery of the 2,3,7,8-TCDD-$^{37}Cl_4$ enrichment efficiency standard and each $^{13}C_{12}$-labeled internal standard, relative to either 1,2,7,8-TCDD-$^{13}C_{12}$ or 1,2,3,7,8,9-HxCDD-$^{13}C_{12}$, is calculated using the following equation:

Equation 9

$$\%R = \frac{Ais \times Qrs \times 100}{Rfr \times Ars \times Qis}$$

Where:
%R = Percent recovery of labeled internal standard
Ais = Sum of integrated areas of labeled internal standard
Qrs = Quantity of recovery standard
Ars = Sum of integrated areas of recovery standard
Rfr = Response factor of the specific labeled internal standard relative to the recovery standard
Qis = Quantity of the labeled internal standard added to the sample.

14.4.8. Calculate the %Difference using Equation 10.

Equation 10

$$\%\,Difference = \frac{RF_1 - RF_c}{RF_1} x100$$

Where:
RF_1=Average response factor from initial calibration.
RF_c=Response factor from current verification check standard

14.4.9. Calculate the %recovery using Equation 11 and the RPD using Equation 12.

Equation 11

$$\text{Percent Recovery} = \frac{C_q}{C_a}(100)$$

Where,
C_q=Quantitated concentration of compound *x* in ppbv;
C_a=Actual concentration of compound *x* in ppbv.

Equation 12

$$RPD = \frac{|R1 - R2|}{\frac{R1 + R2}{2}}(100)$$

where,
R1=result for sample 1
R2=result for sample 2

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See tables in section 11 & 13.

16. Corrective Actions for Out-of-Control Data

16.1. See tables in section 11 & 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. If not specifically listed in the table in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager, Project Manager or analytical staff.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269 – Determination of Limit of Detection and Limit of Quantitation (or equivalent replacement) for each matrix per instrument.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020 - Training Procedures (or equivalent replacement).

18.4. **Periodic performance evaluation (PE)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258 – Proficiency Testing Program (or equivalent replacement). Results are stored in the QA office.

19. Method Modifications

19.1. 8290/8290A Table of Modifications

8290 section	8290A section	Method	Pace SOP
1.2	1.2	8280 Analyses	High level samples are not automatically analyzed by Method 8280.
2.7	2.7	Standards	Method 1613/DLM2.0 standards are substituted for those described in Method 8290.
3.4/4.2	4.4	Second column confirmations	Confirmations are not performed unless specifically required for a project. (Required for Wisconsin Samples)
11.3.1	5.5.1	Samples weighed in hood	Sample may be homogenized in a hood and weighed outside of the hood
7.5	11.5	Chromatographic columns	The sizes for some columns may vary from those listed
4.3.27	6.3.27	Rotary evaporator for concentration	Other options used for concentration
4.2	6.2	DB-5 column specified	May substitute a DB-5MS column
5.2	7.3.3	Silica activated at 180 C	May be activated at 400 C
7.5	11.5	Acid or basic silica options	Neutral silica may be substituted
5.7	7.8	Column performance mix	May be combined with CS-3
7.6	11.6	GC program	The GC program does not match the one in the method
7.8.4.1	11.8.4.1	Minimum retention time	Shorter retention times may be used due to advances in chromatographic columns. This does not apply to DLM2.0.
7.4.5.2	11.4.5.2	Aqueous percent solids	Percent solids determinations are not performed on samples obviously containing less than 1% solids.
7.4.5.1	11.4.5.1	Marking bottle volumes	Since weights are used for sample calculations, the sample volume is not marked.
7	11	Solvent volumes for extraction	Volumes used for sample extraction may vary from those in the method.
7.3.3	8.7	Lipid determination	Lipids may otherwise be determined as described in attachment IX
7.5	11.5	Extract cleanup	Cleanup column preparation and elution volumes were modified from those described in this method.
8.4	--	Laboratory performance	QC outliers may sometimes be flagged and reported depending on project requirements.
3.0	4.0	Interferences	The presence of interferences may be flagged and narrated.
7.9.3	--	Dilution	Samples with levels above the calibration range may be diluted.

19.2. 1613B Table of Modifications

1613B Method	**Pace SOP**
2.1.1.2+ Particulate filtered	Particulate is separated by centrifuge
2.1.2+ SDS used for extraction	Soxhlet is optional substitute for SDS
4.2.2 Glassware washing	Glassware wash sequence is modified
4.2.4 Pre-extraction with toluene	Methylene chloride is an optional substitute for toluene
5.3.1 Samples weighed in hood	Sample are homogenized in a hood and weighed outside of the hood
6.1.1 Bottles are cleaned	Pre-cleaned bottles are an optional substitute
6.7 GPC cleanup	GPC is not currently available at this facility
6.7.4 Chromatographic columns	Some column size varies from those listed
6.8 Rotary evaporator for concentration	Other options used for concentration
6.9 DB-5 column specified	Optionally substitute a DB-5MS column
7.5 Silica activated at 180 C	Silica activated at 400 C
7.5 Acid or basic silica options	Neutral silica is an optional substitute
7.15 Column performance mix	Optionally combined with CS-3
8.2 Solids stored frozen	Stored at 0-6 C
9.5.1 Order of analysis	Blanks are treated like samples and analyzed at any point in a sequence. Some type of blank must be analyzed before samples to demonstrate that the system is clean.
10.1.1 GC program	The GC program does not match the one in the method
10.2.4 Minimum retention time	Advances in chromatographic columns allow shorter retention times.
11.2.1 Aqueous percent solids	Percent solids determinations are not performed on samples obviously containing less than 1% solids.
11.4.2 Marking bottle volumes	Since weights are used for sample calculations, the sample volume is not marked.
12.1 Solvent volumes for extraction	Some sample extraction volumes vary from those in the method.
12.4.1.9 Lipid determination	Lipids are otherwise determined and described in the Lipid Determination SOP.
13. Extract cleanup	Cleanup column preparation and elution volumes were modified from those described in this method. The columns more closely resemble those from Method 8290A.
15. Laboratory performance	Depending on project requirements, QC outliers are sometimes flagged and reported.
16.5 Second column confirmations	Confirmations are not performed unless specifically required for a project.
16.6/18.3 Interferences	The presence of interferences is flagged and narrated (usually per functional group.)
17.5 Dilution	Samples with levels above the calibration range are diluted.
17.6.1.4.1 Reporting limit	Results below the calibration range are reported and flagged as estimated.

19.3. Any modifications made for DLM2.0 need to be approved by the client prior to sample analysis.

20. Instrument/Equipment Maintenance and Troubleshooting

20.1. There is no set schedule for the maintenance listed in this section. It is performed on an as needed basis. Regular preventative maintenance is performed by Pace employees or by the instrument manufacturer. If the instrument needs to be vented, do the following in this order: close the analyzer isolation valve, turn off the source ion gauge, close the source isolation valve, close all source rough pump valves, and allow air into the source chamber through the bleed valve while watching vacuum gauges to ensure leakage does not occur. If any leakage is seen, close the bleed valve and open the main roughing pump valve. Determine the cause of the problem and correct.

20.2. The rough pump oil must be changed if the pump fails to produce a vacuum lower than 10^{-1} mbar or if the pump oil becomes excessively dark. To do so, turn off the ion gauge, isolate and turn off the diffusion pump and allow it to cool. When the diffusion pump is cool, isolate and turn off the rough

pump. Now drain the oil into a waste container and recap the drain. Add oil up to the full line and turn on the pump. When the gurgling sound stops, open the valve to pump on the instrument. After several minutes, turn on the diffusion pump. Wait another 10-15 minutes and turn on the ion gauge. If it is a source linked pump, the source needs to be evacuated.

20.3. Helium gas is used as the carrier gas for HRMS instruments. When this cylinder pressure falls below 500 psi, the tank must be replaced.

20.4. The chromatographic column used for these analyses is the DB-5MS in a 60 meter length. As with any column, these degrade in time. Once this degradation reaches the point where EPA Method 8290 criteria are not met, the column needs to be replaced. Similar results are required for the DB-225 confirmation column.

20.5. The injector liner and baseplate require periodic cleaning or replacement. This maintenance is performed either as a preventative measure or when analyte response factors indicate that injector maintenance is required. A low response factor for the heavier labeled analytes is a typical indicator that injector maintenance is required.

20.6. Air leaks are a common source of problems in mass spectrometry. If the system seems unstable or shows arching, the first step is to check for air leaks. This is done by comparing the signal at m/z 28 to historic levels or by monitoring the mass of a gas or solvent that is then applied to potential leaking locations. Correct any leaks before proceeding to other measures.

20.7. Source/ion volume cleaning is also be done either as a preventative measure or to correct issues with instrument operation. Source cleaning is performed when tuning parameters no longer offer the desired affect, when arcing occurs, or for a number of other reasons. Instructions for removing, cleaning and reassembly of the source are provided in the instrument operation manuals.

20.8. All maintenance must be documented. Routine maintenance, such as injector maintenance, ion volume cleaning, etc. is recorded in the instrument run log. Other 'major' maintenance is documented in the maintenance log that is also incorporated into the log book.

21. Troubleshooting

21.1. Refer to section 20.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Therefore, all PCDDs and PCDFs must be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and who understand the risks associated with this procedure.

22.4. Neat PCDDs and PCDFs require the use of respirators and are <u>not</u> to be handled in the laboratory.

22.5. All samples analyzed at the Minnesota laboratory are held until analytical results have been reported. Samples containing PCDD/PCDFs above the allowable levels are labeled, segregated, and disposed of by personnel trained in handling toxic waste. Similarly grossly contaminated waste items including

pipette tips and other laboratory equipment are segregated, collected in lined waste containers, properly labeled, and disposed of in accordance with hazardous waste regulations.

22.6. Laboratory staff must wipe down a representative area of specified fume hoods at least annually using pre-sterilized gauze and hexane. These wipes must be analyzed according to this method to ensure that good laboratory practices are observed at all times. The results of the wipes must be archived for reference.

23. Waste Management

23.1. All laboratory waste are managed and disposed in accordance with all federal, state, and local laws and regulations. Procedures for handling waste generated during this analysis are addressed in S-MN-S-003 - Waste Handling and Management (or equivalent replacement).

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, “Quality Systems”- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, “Quality Systems”- most current version.

25.4. Department of Defense (DoD) Quality Systems Manual- most current version.

25.5. USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8290A, February, 2007.

25.6. USEPA Method 1613: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (September 1997, Revision B).

25.7. USEPA Analytical Services Branch: Analysis of Chlorinated dibenzo-p-dioxins (CCDs) and Chlorinated Dibenzofurans (CDFs), Method DLM2.0, May 2005.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. ATTACHMENT I – Dioxin Extraction Worksheet (example)

26.2. ATTACHMENT II – GC Program (example)

26.3. ATTACHMENT III – MS Acquisition Program (example)

26.4. ATTACHMENT IV – Method 8290 Analyte List

26.5. ATTACHMENT V – 1613B Acceptance Criteria

26.6. ATTACHMENT VI – Food and Feed Extraction Amounts

26.7. ATTACHMENT VII - Theoretical Ion Abundance Ratios and QC limits

26.8. ATTACHMENT VIII – Additional Requirements for DLM2.0

26.9. ATTACHMENT IX - Process for Lipid Determination

27. Revisions

Document Number	Reason for Change	Date
S-MN-H-001-Rev.26	Table 7.1 – Added "WI Samples. . . -10°C" to Storage for Solid Table 7.1 – Changed from "10°C" to "-10°C" in Storage for Tissue Table 9.1 – Changed "Solvent" to "Acid" under Description for Sulfuric Acid and GW: Nitric Acid Table 9.1 – Added "Sodium Thiosulfate. . . equivalent replacement" Table 9.1 – Added "Avalon. . . current version" Table 10.1 – Added "Canola oil. . . Local grocery store" Table 10.1 – Added Primary Ical Stock Standard Table 10.1 – Added ICV Stock Standard 10.5 – Removed "(AI2 #)" 10.5 Note – Removed "AI2 #", "AI2", and "standard from. . . Preparation Logbook." 10.5.1 – Replaced "Cambridge" with "Cerilliant" 10.5.1 Note – Removed "BI2" 10.5.2 – Replaced "Sonicate" with "Vortex" 10.6 – Removed "(BI2 #)" 10.6.1 – Removed "Sonicate the. . . minutes and", replaced "it" with "the stock standard", added "Vortex for. . . an aliquot." 10.6.2 – Removed "(AI2 #)" 10.6.3 – Removed "(BI2 #)" 10.6.4 – Removed "BI2 #" and replaced "BI2" with "the" 10.6.8 – Removed "(BI2 #)" 10.7 – removed "(AN1 #)" 10.7.1 – Replaced "Cambridge, TerraChem" with "Willington" 10.7.2 – Replaced "Divided the standard. . . and preparer's initials." with "The native stock. . . top amber vial." 10.7.3 – Removed – "AN1 #" and replaced "AN1" with "the" 10.7.4 – Removed "Seal with Teflon tape and" 10.7.5 – Replaced "HRMS Standard" with "Dioxin Stock Standard" 10.8 – Removed (BN1 #) 10.8.1 – Removed "Sonicate. . . five minutes and", and added "Vortex. . . an aliquot." 10.8.2 – Replaced "1.0mL" with "0.275mL", replaced "AN1 #" with "native stock solution", changed "20mL" to "10 mL", changed "20-200ng/mL" to "10-100ng/mL", and removed "A secondary solution. . . on the situation." 10.8.3 – Changed "Sonicate for. . . preparation" to "Vortex for. . . homogenization", and removed "(BN1 #) 10.8.4 – Replaced "BN1" with "FS-N", added "full scan native", and replaced "BN1" with "the" 10.8.5 – Removed "Seal vials with Teflon tape and" 10.9 – Removed "(AC14 #) 10.9.1 – Replaced "Sonicate. . . five minutes" with "Vortex the vial" 10.9.2 – Added "Cleanup stock", and remove "(AC14 #) 10.9.3 – Remove "AC14 #" and replace "AC14" with "the" 10.10 – Removed "(BC14 #) 10.10.1 – Replaced "Sonicate. . . minutes and" to "Vortex the standard and" 10.10.2 – Changed "CSPS (AC14 #)" to "cleanup stock standard" 10.10.3 – Changed "Sonicate. . .minutes" to "Vortex. . . seconds" 10.10.4 – removed "BC14 #" 10.10.5 – Removed "Seal. . . tape and"	10Sep2015

S-MN-H-001-Rev.26	10.11 – Removed "(CC14 #) 10.11.1 – Changed "Sonicate the. . . five minutes" to "Vortex" 10.11.2 – Changed "BC14 #" to "Cl4 Cleanup stock standard" 10.11.3 – Removed "(CC14 #) 10.11.4 – Removed "CC14 #" and replaced "CC14" with "the" 10.11.5 – Chagned "Seal. . . tape" to "Vortex" 10.12 – Removed "(AR2 #)" 10.13 – Removed "(CR3 #)" 10.13.2 – Replaced "AR2 #" with "C_{12} Recovery stock standard" 10.13.3 – Change "Sonicate for five minutes" to "Vortex" and removed "(CR3 #)" 10.13.4 – Removed "CR3 #" and replaced "CR3" with "the" 10.13.5 – Replaced "Seal. . . tape and" with "Store" 12.2 – Added "- See SOP S-MN-O-465. . . options" 12.2.2.3 – Added "three times." 12.1.1.4 – Replaced "Cover all. . . foil, and" with "Bake" 12.1.2 – Added " – optional cleaning" 12.3.1.2 – Added "<9" and "If there is. . . between 7-9." 12.3.1.4 – Added "Allow equilibration for 1 hour with the samples." 12.3.2.6 – Changed "12.13"0 to "12.12" 12.3.3 Note – Added "North and" 12.3.3.3 – Added "such as centrifuge" and removed "heat" 12.3.3.5 – Changed "40mL" to "100mL" 12.3.3.6 – Changed "2 hours" to "4 hours", added "Assemble the round. . . the Snyder column.", and removed "and Snyder" 12.3.3.8 – Replaced "12.13" with "12.12" 12.5.1.1 – Added "Review the percent. . . dry weigh samples." And removed "sample sufficient. . . described above)" 12.5.1.2 – Added this section 12.5.1.3 – Added this section 12.5.1.4 – Used to be 12.5.1.2 and added "Allow the. . . with extraction." 12.5.1.5 – Used to be 12.5.1.3 and added "Allow the. . . with extraction." 12.5.1.4 – Old section is removed 12.5.1.5 – Old section is removed 12.5.1.6.1 – Replaced "If necessary. . .toluene flow." with "Fill the soxhlet. . . 16-24 hours." 12.5.1.6.2 – Added "Continue to" and change "a minimum of 16-24 hours" to "the 16-24 hours" 12.5.1.7 – Used to be 12.5.1.8 and Remove "The extract can. . . a steambath." 12.5.1.7 – Old section is removed 12.5.1.8 – Used to be 12.5.1.9 and add "5" 12.5.1.9 – Used to be 12.5.1.10 and replaced "three" with "~5" 12.5.1.10 – Used to be 12.5.1.11 and changed "12.13" with "12.12" 12.5.2 – Removed entire section 12.6.3 – Added "Allow the. . . with extraction." 12.6.4 – Added "Allow the. . . with extraction." 12.6.11 – Replaced" 12.13" with 12.12" 12.7.1.1 – Added "If the. . . in 12.5" and ", but less than 90% moisture" 12.7.1.2 – Added "Allow the. . . to extraction." 12.7.1.3 – Added "Allow the. . . to extraction." 12.7.2.6 – Changed "12.13" to "12.12" 12.8 – Removed entire section 12.9 – Removed entire section	10Sep2015
SPT QAPP Revision 3	12.8.2 – Added "Allow the. . . with extraction."	April 5, 2016 B-647

S-MN-H-001-Rev.26	12.8.3 – Added "Allow QC. . . with extraction." 12.8.8 – Replaced "Three" with "~5" 12.8.9 – Replaced "12.13" with "12.12" 12.9.2 – Added "Allow the. . . with extraction." 12.9.3 – Added "Allow the. . . with extraction." 12.9.14 – Replaced "12.13" with "12.12" 12.10.3 – Added "Allow the. . . with extraction." 12.10.4 – Added "Allow the. . . with extraction." 12.10.9 – Added this section 12.10.10 – Replaced "The extract. . . steam bath" with "Add 30-50mL. . . bottom flask." 12.10.15 – Removed this section 12.11.1 – Removed ": IE Corn Oil" 12.11.3 – Replaced this entire section 12.11.4 – Replaced "corn" with "canola" and added "Allow the. . . with extraction" 12.11.5 – Changed "1 mL" to "20 µL" and added "Allow the. . . with extraction." 12.11.6 – Replaced this entire section 12.11.7 – Removed "macro scale acid back extraction and" 12.12.1.1 – removed "prior to. . . evap apparatus" 12.12.1.3 – Change "Shake" to "Agitate the samples" 12.12.1.4 – Replaced "12.13" with "12.12" 12.12.1.6 – Replaced "12.13" with "12.12" 12.12.2.1 – removed "(CC14 #)" 12.12.2.3 – Replaced "Shake for two minutes" with "Agitate briefly" 12.12.2.5 – Changed "12.13" with "12.12" and "5% . . . solution" with "DI water" 12.12.3.1 – Changed entire section 12.12.3.2 – Changed entire section 12.12.3.3 – Removed "Rinse the. . . of hexane" 12.12.3.4 – Change "1 cm" to "1/2 inch" 12.12.3.8 – Added section 12.12.3.9 – Changed "50mL" to 60mL" and removed "If carbon. . . of toluene." 12.12.3.10 – Changed "1 mL" to "5-10 mL", added "250 uL", removed "jumbo" 12.14.3.10 – Removed entire section 12.12.4.1 – Changed "12mm" with "15mm" and removed "three times" 12.12.4.2 – Added "and 2 g sodium sulfate" and "allow this to. . . stacked columns" 12.12.4.3 – Removed "(CC14 #) and added "in 12.12.3.10" 12.12.4.5 – Changed "90mL" to 80mL", added "onto the. . . stacked columns" and removed "Collect the. . . mL beaker." 12.14.4.6 – Removed entire section 12.14.4.8 – Removed entire section 12.14.4.9 – Removed entire section 12.12.5.1 – Replaced "12mm" with "15mm" and "1 hour" to "4 hours" 12.12.5.2 – Replaced "10 mL" with 15-20 mL", added "from 12.12.4.2" and removed "Plug the bottom. . . to the air." 12.12.5.3 – Removed "Quantitatively. . . alumina.", Added "The 80 mL. . . silica column then" and changed "35 ml" to "40 ml"	10Sep2015

S-MN-H-001-Rev.26	12.12.5.5 – Changed entire section 12.12.6.1 – Changed entire section 12.12.6.2 – Changed entire section 12.12.6.3 – Changed "12 mm" to "15 mm" and removed "Rinse the. . . of hexane." 12.12.6.4 – Changed "0.5 g" to "1 g" 12.12.6.5 – Replaced "5 mL of toluene. . . and 5 mL of hexane" with "10-15 mL hexane" 12.12.6.6 – Changed "quantitatively transfer. . . of hexane" to "allow the. . . alumina column" 12.12.6.7 – Replaced "If carbon. . . of toluene" with "Proceed to Final Extract Transfer" 12.14.6.9 – Entire section removed 12.14.7 – Entire section removed 12.13.1.4 – Removed "(CR3 #)	10Sep2015

ATTACHMENT I – Dioxin Extraction Worksheet (example)

Dioxin **Water** **Sep Funnel** **EB-15245**

QC Matrix Lot #:
Time of Spiking:
Balance: 10BAL2

Extract Solvents:
Toluene Lot #
Hexane Lot #
MeCl Lot #

Extraction On (Date/Time): 08/27/14 14:00
Extraction Off (Date/Time): 08/27/14 20:00

Standards	Name/ID	Amount	Initial	Witness	Expiration Date
Internal Std.	FS-I-9966-126	20	KH	CMB	07/18/15
Native	FS-N-9966-133	20	KH	CMB	08/07/15
Cl37 Std.	DWCL4-9966-135	250	MF		07/24/15
Recovery	FS-R-9966-136	10	MF		08/20/15
Tridecane	A0341780	10	MF		
Others	FS-I-9966-131	20			08/05/15

#	Sample ID	Internal Standards	Native Standards	Full Bottle Weight	Empty Bottle Weight	pH/ResCl Check	pH Adjusted	Glassware Set	Location	Comments
1	BLANK-41752	x		1492.1	509.3					Extraction QC
2	LCS-41753	x	x	1494.2	509.0					Extraction QC
3	LCSD-41754	x	x	1503.1	509.4					Extraction QC
4	10278321001	x		1106.5	412.0				Rcving	
5	10278610001	x		1573.6	512.7				Rcving	
6	10278439001	x		1387.7	439.0				Rcving	
7	10278508001	x		1487.7	490.8				Rcving	
8	10278821002	x		1378.5	417.5				10/C10 29	
9	10278998001	x		1384.6	417.2				Rcving	
10	10278808001	x		1433.3	438.5				Rcving	
11	10278808002	x		1423.4	438.4				Rcving	
12	10278808003	x		1436.8	438.8				Rcving	
13	10278808004	x		1442.4	439.2				Rcving	
14	10278846001	x		1558.1	567.3				Rcving	
15	10278978001	x		1573.2	514.6				10/C10 29	
16	10278841001	x		1133.9	390.6				Rcving	
17	10278841002	x		1384.6	391.6				Rcving	
18	10278938001	x		1423.3	436.5				Rcving	
19	10278938002	x		1404.4	431.0				Rcving	
20	92213407002A	x		1362.5	406.6					

Relinquished By: M Felea Received By: Date:

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EB-15245

Batch Notes:

Silica
Initials TDP
Date 8/28/2014
Neutral Batch 1
Basic Batch 1
Acid Batch 1
Hexane Lot # 141255
Dispenser

Alumina
Initials MF
Date 8/29/2014
Alumina Lot # 31
Hexane Lot # 141255
Dispenser Q193
60% Batch 1591
Dispenser HRBT-011

Carbon
Initials
Date
Hexane Lot #
Dispenser
50% Batch
Dispenser
75% Batch
Dispenser
Toluene Lot #
Dispenser
Methanol Lot #
Dispenser

Florisil
Initials
Date
Florisil Lot #
Hexane Lot #
Dispenser
6% Batch
Dispenser

Acid Base
Sulphuric Acid Lot #
Base Batch

2 of 2

ATTACHMENT I – Dioxin Extraction Worksheet (example)

Dioxin	Tissue	Soxhlet	EB-15250

QC Matrix Lot #: _____ Extract Solvents: Extraction On (Date/Time): 08/27/14 00:45
Time of Spiking: _____ Toluene Lot # _____ Extraction Off (Date/Time): _____
Balance: 10BAL2 Hexane Lot # _____
MeCl Lot # _____

Standards	Name/ID	Amount	Initial	Witness	Expiration Date
Internal Std.	FS-I-9966-131	20	TDP		
Native	FS-N-9966-133	20	TDP		
Cl37 Std.	DWCL4-9966-135	250	MF		07/24/15
Recovery					
Tridecane					
Others					

#	Sample ID	Internal Standards	Native Standards	Extracted mL or g	Glassware Set	Location	Comments
1	BLANK-41766	x		62.4			Extraction QC
2	LCS-41767	x	x	60.5			Extraction QC
3	LCSD-41768	x	x	60.2			Extraction QC
4	10278349001	x		61.2		Rcving	
5	4099994001	x		20.7		Rcving	
6	4099994002	x		20.1		Rcving	
7	4099994003	x		20.1		Rcving	
8	4099994005	x		16.4		Rcving	
9	4099994006	x		7.2		Rcving	
10	4099994007	x		21.5		Rcving	
11	4099996001	x		20.0		Rcving	
12	4099996002	x		20.2		Rcving	
13	4099996003	x		20.3		Rcving	
14	4099996004	x		14.8		Rcving	
15	4099996005	x		20.6		Rcving	
16	4099996006	x		20.5		Rcving	
17	4099996007	x		20.6		Rcving	
18	4099996008	x		20.4		Rcving	

Relinquished By: _____ Received By: _____ Date: _____

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Batch Notes: EB-15250

Silica		Alumina		Carbon		Florisil	
Initials	MF	Initials	MF	Initials		Initials	
Date	9/3/2014	Date	9/4/2014	Date		Date	
Neutral Batch	10667-2N	Alumina Lot #	31	Hexane Lot #		Florisil Lot #	
Basic Batch	10667-2B	Hexane Lot #	141255	Dispenser		Hexane Lot #	
Acid Batch	10667-2A	Dispenser	Q193	50% Batch		Dispenser	
Hexane Lot #	141255	60% Batch	1592	Dispenser		6% Batch	
Dispenser	Q193	Dispenser	HRBT-011	75% Batch		Dispenser	
				Dispenser			
				Toluene Lot #			
				Dispenser			
				Methanol Lot #			
				Dispenser			

Acid Base
Sulphuric Acid Lot # _____
Base Batch _____

Be sure to include Witness initials, and Expiration dates. This sheet is just an example, but is not in fact complete.

2 of 2

ATTACHMENT II – GC Program (example)

Inlet Method Report MassLynx 4.1 **Page 1 of 2**

Method File: C:\MassLynx\Default.pro\Acqudb\dioxfur
Last Modified: Tuesday, October 13, 2009 12:12:43 Central Daylight Time

Printed: Tuesday, October 13, 2009 12:33:55 Central Daylight Time

HP6890 GC Column 1

Column Length(m)	30.00
Column Diameter(um)	250.00
Film Thickness(um)	0.25
Carrier Gas	HELIUM
Mode	Constant Pressure
Inlet	Front Inlet

HP6890 GC Column 2

Column Length(m)	60.00
Column Diameter(um)	250.00
Film Thickness(um)	0.25
Carrier Gas	HELIUM
Mode	Constant Flow
Inlet	Back Inlet

HP6890 GC Oven Parameters

Maximum Oven Temp(°C)	350.0
Equilibrium Time(min)	0.3

HP6890 GC Oven Ramp

Initial Temperature(°C) 180.0

Time At initial temperature(mins) 3.00

Time(min)	Rate(°C/min)	Temp(°C)
20.0	12.0	226.0
3.5	6.0	320.0
0.0	0.0	24.0
0.0	0.0	24.0
0.0	0.0	24.0
0.0	0.0	24.0

HP6890 GC Pressure 1

Initial Pressure(kPa) 0.1

Time(min)	Rate(kPa/min)	Final Pres(kPa)
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

HP6890 GC Flow 2

Initial Flow(ml/min) 1.0

Time(min)	Rate(ml/min^2)	Final Flow(ml/min)
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

HP6890 PTV Inlet Cryogenic Parameters

Cryo Cooling Enabled
Ambient Temperature(°C) 40.0

Back Inlet
Split/Splitless: Splitless Mode

Initial Temperature(°C)	280.0
Initial Pressure(kPa)	1.0
Purge Pressure(kPa)	20.0
Purge Time(min)	1.00

ATTACHMENT III - MS Acquisition Program (example)

AutoSpec Experiment Report Page 1

Experiment File: c:\masslynx\default.pro\acqudb\dioxfur.exp

Printed : Thu Jan 13 10:26:46 2005

Name	Default Experiment
Creation Time	Thu 13 Jan 2005 10:06:51
Instrument Identifier	Autospec
Version Number	1.0
Duration (min)	46.0
Solvent Delay Divert Valve Enabled	0
Number Of Functions	5

Function 1 : Voltage SIR, Time 12.00 to 29.20, Mass 303.90 to 409.80 EI+

Type	Voltage SIR			
Data Format	Centroid			
Ion Mode	EI Mode			
Polarity	Positive			
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW1_10K.ipr			
Start Mass	303.9			
End Mass	409.8			
Start Time (min)	12.0			
End Time (min)	29.2			
Scan Time (sec)	915.0			
InterScan Time (sec)	0.1			
Scans To Sum	1000000			
Number of channels	15			
Channel 0 Mass	303.901600	50.00	15.00	
Channel 1 Mass	305.898700	50.00	15.00	
Channel 2 Mass	315.941800	50.00	15.00	
Channel 3 Mass	317.938900	50.00	15.00	
Channel 4 Mass	318.979200	50.00	15.00	
Channel 5 Mass	318.979200	50.00	15.00	LM
Channel 6 Mass	319.896500	50.00	15.00	
Channel 7 Mass	321.893600	50.00	15.00	
Channel 8 Mass	327.884700	50.00	15.00	
Channel 9 Mass	331.936700	50.00	15.00	
Channel 10 Mass	333.933800	50.00	15.00	
Channel 11 Mass	339.859700	50.00	15.00	
Channel 12 Mass	341.856700	50.00	15.00	
Channel 13 Mass	375.836400	20.00	15.00	
Channel 14 Mass	409.797400	20.00	15.00	

Function 2 : Voltage SIR, Time 29.20 to 34.80, Mass 339.86 to 409.80 EI+

Type	Voltage SIR
Data Format	Centroid
Ion Mode	EI Mode
Polarity	Positive
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW2_10K.ipr
Start Mass	339.9
End Mass	409.8
Start Time (min)	29.2
End Time (min)	34.8
Scan Time (sec)	840.0
InterScan Time (sec)	0.1
Scans To Sum	1000000
Number of channels	12

ATTACHMENT III (Continued)

AutoSpec Experiment Report Page 1

Experiment File: c:\masslynx\default.pro\acqudb\dioxfur.exp

Printed : Thu Jan 13 10:26:46 2005

Name	Default Experiment
Creation Time	Thu 13 Jan 2005 10:06:51
Instrument Identifier	Autospec
Version Number	1.0
Duration (min)	46.0
Solvent Delay Divert Valve Enabled	0
Number Of Functions	5

Function 1 : Voltage SIR, Time 12.00 to 29.20, Mass 303.90 to 409.80 EI+

Type	Voltage SIR			
Data Format	Centroid			
Ion Mode	EI Mode			
Polarity	Positive			
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW1_10K.ipr			
Start Mass	303.9			
End Mass	409.8			
Start Time (min)	12.0			
End Time (min)	29.2			
Scan Time (sec)	915.0			
InterScan Time (sec)	0.1			
Scans To Sum	1000000			
Number of channels	15			
Channel 0 Mass	303.901600	50.00	15.00	
Channel 1 Mass	305.898700	50.00	15.00	
Channel 2 Mass	315.941800	50.00	15.00	
Channel 3 Mass	317.938900	50.00	15.00	
Channel 4 Mass	318.979200	50.00	15.00	
Channel 5 Mass	318.979200	50.00	15.00	LM
Channel 6 Mass	319.896500	50.00	15.00	
Channel 7 Mass	321.893600	50.00	15.00	
Channel 8 Mass	327.884700	50.00	15.00	
Channel 9 Mass	331.936700	50.00	15.00	
Channel 10 Mass	333.933800	50.00	15.00	
Channel 11 Mass	339.859700	50.00	15.00	
Channel 12 Mass	341.856700	50.00	15.00	
Channel 13 Mass	375.836400	20.00	15.00	
Channel 14 Mass	409.797400	20.00	15.00	

Function 2 : Voltage SIR, Time 29.20 to 34.80, Mass 339.86 to 409.80 EI+

Type	Voltage SIR
Data Format	Centroid
Ion Mode	EI Mode
Polarity	Positive
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW2_10K.ipr
Start Mass	339.9
End Mass	409.8
Start Time (min)	29.2
End Time (min)	34.8
Scan Time (sec)	840.0
InterScan Time (sec)	0.1
Scans To Sum	1000000
Number of channels	12

ATTACHMENT III (Continued)

AutoSpec Experiment Report Page 3

Experiment File: c:\masslynx\default.pro\acqudb\dioxfur.exp

Printed : Thu Jan 13 10:26:46 2005

Channel 0 Mass	380.976000	50.00	20.00	
Channel 1 Mass	380.976000	50.00	20.00	LM
Channel 2 Mass	407.781800	50.00	20.00	
Channel 3 Mass	409.778800	50.00	20.00	
Channel 4 Mass	415.000000	30.00	20.00	
Channel 5 Mass	417.825000	50.00	20.00	
Channel 6 Mass	419.822000	50.00	20.00	
Channel 7 Mass	423.776700	50.00	20.00	
Channel 8 Mass	425.773700	50.00	20.00	
Channel 9 Mass	430.000000	30.00	20.00	
Channel 10 Mass	435.816900	50.00	20.00	
Channel 11 Mass	437.814000	50.00	20.00	
Channel 12 Mass	479.716500	50.00	20.00	

Function 5 : Voltage SIR, Time 43.00 to 46.00, Mass 429.97 to 513.68 EI+

Type	Voltage SIR
Data Format	Centroid
Ion Mode	EI Mode
Polarity	Positive
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW5_10K.ipr
Start Mass	430.0
End Mass	513.7
Start Time (min)	43.0
End Time (min)	46.0
Scan Time (sec)	875.0
InterScan Time (sec)	0.1
Scans To Sum	1000000

Number of channels	13			
Channel 0 Mass	429.972800	50.00	15.00	
Channel 1 Mass	430.972800	50.00	15.00	LM
Channel 2 Mass	430.972800	50.00	15.00	
Channel 3 Mass	441.742800	50.00	15.00	
Channel 4 Mass	443.739800	50.00	15.00	
Channel 5 Mass	453.783000	50.00	15.00	
Channel 6 Mass	455.780100	50.00	15.00	
Channel 7 Mass	457.737700	50.00	15.00	
Channel 8 Mass	459.734700	50.00	15.00	
Channel 9 Mass	465.000000	80.00	15.00	
Channel 10 Mass	469.777900	50.00	15.00	
Channel 11 Mass	471.774900	50.00	15.00	
Channel 12 Mass	513.677500	50.00	15.00	

ATTACHMENT IV - Method 8290 Analyte List

Compound	CAS Registry No.[a]
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin (PeCDD)	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin (HxCDD)	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin (HpCDD)	35822-46-9
1,2,3,4,5,6,7,8-Octachlorodibenzo-*p*-dioxin (OCDD)	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	55673-89-7
1,2,3,4,5,6,7,8-Octachlorodibenzofuran (OCDF)	39001-02-0
Total Tetrachlorodibenzo-*p*-dioxin (TCDD)	41903-57-5
Total Pentachlorodibenzo-*p*-dioxin (PeCDD)	36088-22-9
Total Hexachlorodibenzo-*p*-dioxin (HxCDD)	34465-46-8
Total Heptachlorodibenzo-*p*-dioxin (HpCDD)	37871-00-4
Total Tetrachlorodibenzofuran (TCDF)	55722-27-5
Total Pentachlorodibenzofuran (PeCDF)	30402-15-4
Total Hexachlorodibenzofuran (HxCDF)	55684-94-1
Total Heptachlorodibenzofuran (HpCDF)	38998-75-3

[a] Chemical Abstract Service Registry Number

ATTACHMENT V – 1613B Acceptance Criteria

A. Acceptance Criteria for Performance Tests When All CDDs/CDFs are Tested[1]

CDD/CDF	Test Conc. (ng/mL)	s (ng/mL)	IPR[2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-56
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,7,8,9-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	20-186	77-129
$^{13}C_{12}$-OCDD	200	95	41-276	26-397	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1	7.9-12.7

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT V – 1613B Acceptance Criteria (Continued)

B. Acceptance Criteria for Performance Tests When Only Tetra Compounds are Tested [1]

CDD/CDF	Test Conc. (ng/mL)	s (ng/mL)	IPR[2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.7	8.7-12.4	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	2.0	9.1-13.1	8.0-14.7	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32-115	25-141	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35-99	26-126	76-131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5-13.4	3.7-15.8	8.3-12.1

C. Labeled Compound Recovery in Samples When All CDDs/CDFs are Tested

CDD/CDF	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL)[1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138	26-138
$^{13}C_{12}$-OCDD	200	34-313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5-19.7	35-197

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT V – 1613B Acceptance Criteria (Continued)

D. Labeled Compound Recovery in Samples When Only Tetra Compounds are Tested

CDD/CDF	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL)[1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT VI – Food and Feed Extraction Amounts

Food and Feed Extraction Amounts, 10 µL Final Volume

Food or Feed Type	EU Limit	Target PQL	Amount	Weight Basis
Meat, Ruminants	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Meat, Poultry	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Meat, Pig	0.6 pg/g	0.12 pg/g	35 grams	Lipid
Meat, Liver	4.0 pg/g	0.8 pg/g	10 grams	Lipid
Fish, Muscle	3.0 pg/g	0.6 pg/g	15 grams	Lipid
Milk/Milk Products	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Eggs/Egg Products	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Oils & Fats, Ruminants	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Oils & Fats, Poultry	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Oils & Fats, Pigs	0.6 pg/g	0.12 pg/g	35 grams	Lipid
Oils & Fats, Mixed	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Vegetable Oil	0.5 pg/g	0.1 pg/g	40 grams	Lipid
Fish Oil	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Fruits	0.4 pg/g	0.08 pg/g	100 grams	Total
Vegetables	0.4 pg/g	0.08 pg/g	100 grams	Total
Cereals	0.4 pg/g	0.08 pg/g	100 grams	Total
Feed Materials, Plant	0.5 pg/g	0.1 pg/g	80 grams	Total
Minerals	0.5 pg/g	0.1 pg/g	80 grams	Total
Animal Fat, Incl. Milk & Eggs	1.2 pg/g	0.24 pg/g	34 grams	Total
Animal Products	0.5 pg/g	0.1 pg/g	80 grams	Total
Fish Oil	4.5 pg/g	0.9 pg/g	10 grams	Total
Fish	1.0 pg/g	0.2 pg/g	40 grams	Total
Compound Feedstuffs	0.4 pg/g	0.08 pg/g	100 grams	Total
Pet Food	1.5 pg/g	0.3 pg/g	28 grams	Total

ATTACHMENT VII - Theoretical Ion Abundance Ratios and QC limits

Theoretical Ion Abundance Ratios and QC Limits				
Number of Chlorine Atoms	**M/Z's Forming Ratio**	**Theoretical Ratio**	**QC Limit[1] Lower**	**Upper**
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
5[3]	M/(M+2)	0.61	0.52	.70
6	(M+2)/M+4)	1.24	1.05	1.43
6[4]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7[5]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

1 QC limits represent ±15% windows around the theoretical ion abundance ratios.

2 Does not apply to the clean up standard ($^{37}Cl_4$-2,3,7,8-TCDD)

3 used for native PeCDD only

4 used for $^{13}C_{12}$-HxCDF Only

5 used for $^{13}C_{12}$-HpCDF Only

ATTACHMENT VIII – Additional Requirements for DLM2.0

Requirements for DLM2.0 Projects*

Samples must be extracted within 10 days of collection, except for CWA and SDWA waters which are extracted within 7 days. The hold time from extraction to analysis is 30 days.

Retention times from each continuing calibration determination must be within 15 seconds of those from the initial calibration.

The retention time for 1,2,3,4-TCDD must be greater than 25 minutes.

Blank levels must be less than the CS1 concentration, except for OCDD and OCDF that must be less than three times higher than in the CS1.

Sample extracts with concentrations above the calibration range must be diluted to bring the analytes within the calibration range. This does not apply to OCDD or OCDF. The dilutions must be made using the internal standard spiking solution.

Dilutions must be less than 20X. If analytes remain above the calibration range after dilution, the sample extraction must be repeated using a smaller sample aliquot.

Re-extract the affected sample if any internal standard recoveries or isotope ratios are outside target ranges. The ranges are those from Method 1613B.

The criterion for an acceptable initial calibration is that native analytes have relative standard deviations of less than 20%. The range is extended to 35% labeled analytes.

The criterion for an acceptable initial calibration is that native analytes have response factors within 20% of the initial calibration curve. The range is extended to 35% labeled analytes.

The LCS recovery criteria are the statistical ranges from Method 1613, however, up to 3 compounds are allowed to have recoveries outside the specified ranges.

Both the column performance mix and continuing calibration must be run at the beginning and end of each analytical sequence and must pass all method requirements. The ending standard analyses must be injected within 12 hours of the sequence start time.

The method blank must be run in each analytical before any of the associated samples. If samples are analyzed in multiple sequences, the associated method blank is analyzed in each sequence.

* Some of these requirements were also noted in the body of this SOP.

ATTACHMENT IX - Process for Lipid Determination

Option 1: Lipid Determination through Soxhlet Extraction

- Tare 40 mL vials using a four-place balance. Record these tare weights in the percent lipids logbook.
- Record the initial weights used to set up the samples for extraction in the percent lipids logbook.
- After Snyder concentration of extracts, transfer extracts to tared 40 mL vials per applicable method SOP.
- Concentrate the transferred extracts in tared 40 mL vials using a nitrogen evaporator until all solvent has evaporated and only lipid is remaining.
- Record final weights of vials and lipids measured using a four place balance in percent lipids logbook.

Option 2: Lipid Determination Using Methylene Chloride

- Accurately weigh out a 10-gram aliquot of sample material using an analytical balance. Record the weight to four places in the lipids logbook (see Attachment I). Use 10% corn oil mix for the laboratory spike matrix.
- Combine sample aliquot with sodium sulfate and stir until the mixture is free flowing (typically 40-60 grams of sodium sulfate are required).
- Set up the glass column and place a plug of glass wool at the bottom. Check that the stopcock is in the closed position.
- Quantitatively transfer the sample/sodium sulfate mixture to the glass column.
- Add 90-mL of methylene chloride to the column and assure the entire sample has been saturated with the solvent. Allow the column to stand for 10 minutes.
- Weigh a 150 mL glass beaker (or equivalent) using an analytical balance and record the tare weight to four places in the lipids logbook under TW. Place the tared glass beaker under the glass column.
- Open the stopcock to allow the methylene chloride to elute from the column at a rate of approximately one drop per second.
- Allow the methylene chloride in the beaker to evaporate to dryness under ambient conditions.
- Reweigh the beaker containing the dried residue on an analytical balance. Record the final weight (FW) to thousandths in the lipids logbook.

QC Requirements

1. This process requires an analytical balance calibrated to the nearest 0.001 gram
2. One method blank is required with each batch of up to 20 samples. Use solvent only for the method blank to insure the process is free from possible contamination
3. Two laboratory control samples, or one LCS and one Sample Duplicate are required for each batch of lipid determination. Use 10 grams of tissue reference material for the LCS/LCSD.

STANDARD OPERATING PROCEDURE

EXTRACTION AND CLEANUP OF PCBS BY MICROWAVE EXTRACTION

Reference Methods: EPA Method 3546

SOP Number:	S-NY-O-280-rev.07
Effective Date:	02/02/16
Supersedes:	S-NY-O-280-rev.06

APPROVALS

Assistant General Manager	02/02/16 Date
Quality Manager	02/02/16 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

This is **COPY#** _____ Distributed on _____ by _____ and is ____ **CONTROLLED**

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1. Purpose/Identification of Method

1.1. This is a Standard Operating Procedure (SOP) for the extraction and cleanup of samples for Polychlorinated Biphenyls (PCBs) using SW-846 EPA Method 3546 (Microwave Extraction) and subsequent analysis by SW-846 Method 8082A.

2. Summary of Method

2.1. Solid samples are weighed, mixed with drying agent, and loaded into a microwave vessel.

2.2. Samples are spiked with the appropriate standards, and solvent is added to the vessel.

2.3. The vessels are sealed and samples are extracted in the microwave and allowed to cool.

2.4. Sample extracts are filtered, concentrated, set to a final volume, and put through a series of cleaning steps.

2.5. Extracts are then submitted for analysis.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of samples for PCB analysis by microwave extraction method 3546.

3.2. **Parameters**: See analytical SOPs for specific analyte lists.

4. Applicable Matrices

4.1. This method is validated for solid, soil, sediment, and sludge samples.

4.2. The working range is 10-11g of sample.

5. Limits of Detection and Quantitation

5.1. Please see determinative method SOPs (S-NY-O-148, S-NY-O-314 current revisions).

6. Interferences

6.1. Laboratory contaminants may be introduced during extraction and subsequent cleanup procedures. The extraction technician should exercise great caution that the equipment used is scrupulously cleaned to prevent contamination of other samples.

6.2. Chlorinated pesticides such as DDT and DDE, sulfur-containing compounds in petroleum products, and plasticizers (phthalate esters) from gloves, tubing, pipette bulbs, coating on clamps, etc. can interfere with PCB quantification.

6.3. Please refer determinative method SOPs (S-NY-O-148, S-NY-O-314 current revisions) for further details of interferences.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Solid samples should be collected in 4 oz. or 8 oz. jars with Teflon lined lids.

7.2. All solid samples should be stored in the walk-in refrigerator at >0-6°C before extraction.

7.3. Extraction of solid samples by appropriate technique must be completed within one year from sample collection. Sample extracts must be analyzed within forty days from extraction.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

8.2. **Accuracy** – The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator..

8.3. **Batch** – Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same quality systems matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours..

8.4. **Method Blank (B)** - A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. Sodium sulfate is processed as blank matrix.

8.5. **Lab Control Sample (LCS)** - Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to evaluate the performance of all or a portion of the measurement system. Sodium sulfate is processed as the LCS.

8.6. **Matrix Spike (MS) -** A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of sample for which an independent test result of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

8.7. **Matrix Spike Duplicate (MSD) –** A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte..

8.8. **Method Detection Limit (MDL)** – The minimum constituent concentration that can be measured and reported with 99% confidence that the signal produced is different from the blank in a given matrix.

8.9. **SDS – Safety Data Sheet. OS**HA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication program**s.**

8.10. **Precision** – The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

8.11. **Quality Control-** The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; also the system of activities and checks used to ensure that measurement systems are

maintained within prescribed limits, providing protection against “out of control” conditions and ensuring that the results are of acceptable quality.

8.12. **Surrogate**: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Microwave:

9.1.1. ETHOS EX , Milestone.

9.1.2. PRO-24 high throughput rotor.

9.1.3. ACPU-TR40 Pressure Reactor.

9.1.4. APCU-140 Thermowell 140mm.

9.1.5. ATC-FO Sensor (FO30009).

9.2. Glass Microwave Insert: 55mL capacity, Milestone P/N 890003:

9.3. Vials with PTFE screw-caps: glass, 40mL and 4 dram, for sample extracts.

9.4. Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.5. Wrist Shaker: Burrell wrist action shaker, Model 75 and 88 (or equivalent).

9.6. Analytical Balance: Mettler PL-303 used to determine sample mass, capable of weighing 0.01g (Or equivalent).

9.7. Filter paper: Advantec P/N NO5A12.5CM 12.5cm.

9.8. UCT Universal Cartridge: United Chemical Technologies p/n ERFV00UNIP (or equivalent).

9.9. Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipette storage.

9.10. Pipettes: S/P Disposable Serological Borosilicate Pipettes:

9.10.1. 1mL X 1/10 #P4650-11X.

9.10.2. 5mL X 1/10 #P4650-15.

9.10.3. 10mL X 1/10 #P4650-110.

9.10.4. Kimble Pasteur Borosilicate glass pipette 9" #72050 (or equivalent).

9.11. Glass or polypropylene funnels (or equivalent).

9.12. Volumetric flasks- 25mL Kimax class A (+/- 0.03ml at 20C) used to set extract volume.

9.13. Aluminum weigh pan: Krackeler Scientific P/N #64-D70-100-PK.

9.14. Kimwipes: Kimtech Kimberly-Clark or equivalent.

9.15. Metal spatula.

9.16. Mixing Tray: Used to mix sample prior to weighing sample.

9.17. Turbo Vap Evaporator: Zymark #ZW640-3 (or equivalent).

9.18. Turbo Vap Evaporator concentrator tubes: Zymark 250mL, 0.5mL endpoint (or equivalent).

9.19. PowerVap Evaporator: Fluid Management Systems (or equivalent).

9.20.

10. Reagents and Standards

10.1. Hydromatrix: UTC P/N EC56603K drying agent or equivalent.

10.2. Hexane: P/N CS219-200 Honeywell Burdick & Jackson. (or equivalent)

10.3. Acetone: P/N CS011-200 Honeywell Burdick & Jackson. (or equivalent)

10.4. 3:1 Hexane/Acetone: 75%:25% by volume solvent mixture, prepared in the lab.

10.5. Spike standard solution: PCB Aroclor in acetone at 10.0ug/mL, 12.5ug/mL, or 100ug/mL in acetone.

10.5.1. To make an A1221/A1242 at 10.0ug/mL GEHR spike: Allow the Stock Standard Solution (SOP S-NY-O-148) to warm up to room temperature. Using a gastight syringe, add 0.75mL of A1221 and 0.25mL of A1242 to a 100mL volumetric flask and set to volume with acetone. All information is recorded in the Standards logbook and LIMS.

10.5.2. To make a 12.5ug/mL Aroclor spike: Allow the Stock Standard Solution (SOP S-NY-O-314) to warm up to room temperature. Using a gastight syringe, add 1.25mL of the Stock Standard Solution to a 100mL volumetric flask and set to volume with acetone. All information is recorded in the Standards logbook and LIMS.

10.5.3. To make a 100ug/mL Aroclor spike: Allow the Stock Standard Solution (SOP S-NY-O-314) to warm up to room temperature. Using a volumetric pipette, add 10mL of the Stock Standard Solution to a 100mL volumetric flask and set to volume with acetone. All information is recorded in the Standards logbook and LIMS.

10.6. Surrogates Standards: Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP)TCMX/DCBP at 0.5/5.0ug/mL in acetone.

10.6.1. To make this standard an ampoule of Custom Standard CUS-4911 (Ultra Scientific) is brought to room temperature and shaken on a wrist action shaker for at least 30 minutes. Once the standard is room temperature 1mL is added to a 1L volumetric flask and set to volume with acetone. All information is recorded in the Standards logbook and LIMS.

10.7. Sodium sulfate (Na_2SO_4): granular, anhydrous; Purify by heating at 400^{o}C for 4 hours. Store unused portion of sodium sulfate in a desiccator. (12-60 mesh). Used as blank matrix.

11. Calibration and Standardization

11.1. The analytical balance should be calibrated daily to ensure accurate measurements are made when weighing solid samples for extraction.

12. Procedure

12.1. **Sample Preparation**:

12.1.1. Throughout the entire process it should be noted that if the technician encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the logbook section in the Laboratory Information Management System (LIMS).

12.1.2. Before any steps are taken, the technician should first review the sample job in the LIMs extraction section. The technician should also verify the sample IDs on the bottle against the chain of custody. If there is a discrepancy on either the sample label or the chain of custody, this should be brought to the attention of a supervisor.

12.1.3. If the sample is sediment and contains a water layer, decant and discard the layer as aqueous PCB waste; document this in the comments section of the bench sheet. Mix the sample thoroughly in the sample container. If there is not enough room to mix sample in the container then remove the entire sample from container, using a metal spatula, into a mixing tray. Mix the sample thoroughly and discard any foreign objects such as sticks, rocks or leaves and document removal of foreign objects in the comments section of the bench sheet. See SOP S-NY-O-347 Sample Homogenization and Sub-Sampling current revision for additional information on proper homogenization and mixing of samples. Note however that the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

12.1.4. If the PCB concentration is to be determined on a dry weight basis, the percent total solid must be determined. See SOP S-NY-I-090 (Determination of Percent Solid in Soils).

12.2. **Sample Extraction:**

12.2.1. Weigh 10g to 11g of previously homogenized sample, taking into consideration moisture content, into a tared 4oz jar using a metal spatula. Use sodium sulfate as the sample for the Method Blank and the Lab Control Sample. Record each weight in LIMS. The Method Blank and LCS **MUST** undergo all steps that the samples go through. Therefore at this stage an aliquot of hydromatrix must be added to these samples before they are extracted.

12.2.2. Mix the sample with enough drying agent (hydromatrix) to dry it. Mix the sample and drying agent until a homogenous sample is obtained; the sample should be free-flowing with no clumps. The amount of drying agent needed depends on the sample matrix and amount of water present in the sample.

12.2.3. Place the dried sample into a hexagonal weighing boat which is used to aid transfer of the sample into a previously labeled microwave glass insert. Add the dried extract to the glass insert using the metal spatula to guide the sample into the cell. This step should be completed for all samples and quality control samples.

12.2.4. Before loading the sample contained in the glass insert into the microwave cell, the cells must be prepped. To prepare the cell, rinse the inside of all Teflon cell pieces with hexane and allow to air dry in the hood.

12.2.5. Inspect the Teflon cap to ensure the edges are not curved over. If the edges are curved over, the Teflon cap must be reshaped using the reshaping tool. Place the cell cap into the cell stretching tool and pull down the lever. Press down with some resistance to stretch the cap, then lift up the lever and remove the cell cap. This will ensure a proper seal on the cell.

12.2.6. Place the Teflon cell body into the outer brown cell shell. Add 5mL of 3:1 hexane/acetone to each Teflon cell. Place the glass insert containing the sample into the Teflon cell body. **Note: The sample with the most complex matrix and water content should be loaded into the cell labeled "ATC". If samples are all about the same, load any sample into the cell labeled "ATC". Never place a Method Blank or LCS into the "ATC" cell.**

12.2.7. Add the appropriate amounts of surrogate and matrix spiking compounds into the glass insert directly onto the sample.

12.2.8. Add approximately 25mL of 3:1 hexane/acetone to each cell.

12.2.9. Fit the stretched Teflon cap into the top of the cell. For the ATC cell only, gently place a hexane pre rinsed Thermowell into the cell through the Teflon cap and push it down until it fits snuggly against the Teflon cap. Extra care should be taken with this step as the Thermowell is made of ceramic and is very fragile. The extraction will not progress properly if the Thermowell is cracked or damaged in anyway, so inspect it thoroughly before use.

12.2.10. Assemble the cap of the cell shell by first placing a Teflon washer and then a Teflon screw into the cap. Screw the assembled cap onto the outer shell body and hand tighten. Do this for all cells except for the ATC cell. It will be assembled later.

12.2.11. Place the PRO-24 high throughput rotor onto the open door of the microwave. Load the rotor with cells, spacing them equidistance from each other if you are able.

12.2.11.1. NOTE: To prevent contamination between samples, make sure the vent hole of each cap is not facing the vent hole of another cap directly next to it. The outer row of cells should have the vent holes facing outwards and the inner row should be facing inwards.

12.2.12. Carefully thread the fiber optic probe through the loop at the roof of the microwave, through the ATC shell cap and Teflon washer, and into the Thermowell. Ensure not to kink or damage the probe. Hand-tighten the ATC shell cap onto the ATC cell and press the probe into place in the cap.

12.2.13. Place the rotor cover onto the top of the rotor and cells. Gently place the rotor into the microwave and set it onto the twist spindle, turning the rotor until it lines up and fits onto the twist spindle. Close the door to the microwave before proceeding.

12.2.14. Load the appropriate method (pcb_115C), checking the times and temperatures, and hit start. See Attachment II. Once started, document the method in the appropriate column in the LIMs program.

12.2.15. After the extraction method has completed, the cells need to cool to room temperature before they can be opened. The cells can cool completely in the microwave, or once the cells are cool enough to be handled, they can be removed and allowed to cool on a bench, in a refrigerator, or in an ice bath. It is important that the samples have cooled at least room temperature before moving to the next step.

12.2.16. After samples have cooled, they will be ready for filtering. There are two methods of filtering microwave samples that is employed at Pace Analytical. One method is gravity powder funnel, and the other method is vacuum filtration using cartridges containing sodium sulfate. The vacuum filtration is suggested for use on samples requiring a very quick turnaround time.

12.3. **Vacuum Filtration:**

12.3.1. For this method, samples will be filtered into 60mL VOA vials as opposed to Turbo Tubes. Set up one vial for each sample and label it with the sample ID.

12.3.2. Place 60mL rinse vials (these can be reused for all rinses) into the vacuum box into a white rack below each filtering station that is going to be used. Rinse each station with approximately 5 mL of acetone and then 5mL of hexane.

12.3.3. Remove rinse vials and place the sample ID labeled 60mL VOA vials inside.

12.3.4. Place the top onto the vacuum box, verify it is secure. If it is not secure, a vacuum will not be created. Also verify that all vials are lined up perfectly under each filtering station spout to ensure sample is filtered into the vial.

12.3.5. Place one cartridge into the placeholder on the top of the vacuum box.

12.3.6. Fill each cartridge with approximately 5g of sodium sulfate (about ¼ full).

12.3.7. Turn vacuum pump switch to the “on” position.

12.3.8. Unscrew the microwave cell shell and set aside the top. Remove the Teflon cap and set aside.

12.3.9. Using tweezers, pull the glass insert out of the cell shell. Rinse down the sides of the insert into the Teflon cell with approximately 1-2mL of hexane.

12.3.10. Carefully pour the contents of the glass insert into the cartridge, rinsing the lip of the insert with hexane.

12.3.11. Rinse the inside of the glass insert with approximately 1-2mL of hexane and pour into the cartridge. Repeat this for a total of three times for each cell.

12.3.12. Pour the remaining solvent from the Teflon cell into the cartridge. Rinse the Teflon cell with approximately 1-2mL of hexane and pour into the cartridge.

12.3.13. Rinse the sodium sulfate with hexane until there is a final volume of approximately 50mL in the vial.

12.3.14. Each station must be rinsed again before another sample can be filtered on it or before putting the filtration system away for the day. See 12.3.2.

12.4. **Powder Funnel** (**Note:** This method of filtration is only to be used if cartridges are not available to perform the vacuum filtration. This section is only followed if you are NOT putting the samples through a vacuum filtration system).

12.4.1. Using a polypropylene funnel, place a folded paper filter into the funnel and fill with sodium sulfate. Place this assembled powder funnel on top of a hexane pre-rinsed and properly labeled turbo tube in a single turbo tube holder. Do this for each sample and quality control sample.

12.4.2. Unscrew the microwave cell shell and set aside the cap. Remove the Teflon cap and set aside.

12.4.3. Using tweezers, pull the glass insert out of the cell shell. Rinse down the sides of the insert into the Teflon cell with approximately 1-2mL of hexane.

12.4.4. Carefully pour the contents of the glass insert into the powder funnel, rinsing the lip into the powder funnel.

12.4.5. Rinse the inside of the glass insert with approximately 1-2mL of hexane and pour into the funnel**.** Repeat this for a total of three times for each cell.

12.4.6. Pour the remaining solvent from the Teflon cell into the funnel. Rinse the Teflon cell with approximately 1-2mL of hexane and pour into the funnel.

12.4.7. Rinse the powder funnel with hexane until there is a final volume of approximately 50mL in the turbo tube.

12.5. **Solvent Reduction: TurboVap/PowerVap Evaporator:**

12.5.1. The TurboVap evaporator system is used in place of the Kuderna Danish (KD) concentrator apparatus. The TurboVap evaporator system is used to reduce the sample volume. The TurboVap uses a heated water bath and positive pressure nitrogen flow with vortex action. The PowerVap uses a heated aluminum block as well as positive pressure nitrogen flow/vortex action Both units maintain a slight equilibrium imbalance between the liquid and the gaseous phase of the solvent extract, which allows fractional reduction of the solvent without loss of higher boiling point analytes.

12.5.2. Turn the unit on and allow it to heat up to 40ºC ± 2ºC. If using the PowerVap, turn on and allow it to heat up to 60 ± 2°C.

12.5.3. As a precaution both system regulators should be checked to insure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the

apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples. To bleed the system of residual gas pressure, place an empty TurboTube or 60mL vial into the unit and close lid. Make sure that the nitrogen gas pressure regulator is closed. Bleed any residual gas until the regulator gauge reads "0" psi. Remove the empty TurboTube or 60mL vial.

12.5.4. Rinse each tip and wipe down all surfaces of the TurboVap/PowerVap with hexane. Close the lid and turn the pressure up to blow the lines clean. Turn off the pressure and bleed the system of any residual gas.

12.5.5. Place TurboTubes or 60mL vials containing the sample extract into TurboVap/PowerVap and close lid. Slowly open the pressure regulator. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

12.5.6. **DO NOT** leave the unit unattended as extracts may be blown to dryness and loss of semi-volatiles as well as surrogate and matrix spike may occur. Immediately notify the extraction supervisor if an extract is blown to dryness and note the incident in LIMS.

12.5.7. Concentrate the solvent to approximately 10mL. Remove the samples from the TurboVap/PowerVap and place in the rack. The remaining solvent will consist largely of hexane since the acetone component is fractionally removed at a faster rate than hexane.

12.5.8. Quantitatively transfer the sample extract into a class A volumetric flask (25mL is the default extract set volume). Rinse the vial or Turbo Tube with hexane and then transfer the hexane rinse to the volumetric. Repeat this until enough hexane has been added to the volumetric meniscus mark. Decant the contents into a pre-labeled 40mL vial.

12.5.9. All dirty glassware and Teflon pieces of the microwave cells must be rinsed with acetone and dried in the fume hood before being washed.

12.6. Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection, contain co-extracted interfering substances which must be removed before accurate chromatographic analysis can be performed. See separate cleanup SOPs for details (S-NY-O-337, S-NY-O-338, S-NY-O-339 and S-NY-O-340, as applicable).

12.7. **Extract Screening and Dilution**

12.7.1. Screening of PCB extracts by GC to determine the approximate concentration before final analysis is highly recommended. If possible, prior site history and estimates of sample concentration will be provided by field personnel and may be used to determine what, if any, extract dilution is necessary.

12.7.2. The supervising technician or supervisor is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of hexane. Dilutions must be recorded in the instrument logbook or in the data system.

12.7.3. Typically 1.0mL of the sample extract is added to 9.0mL of hexane to perform a 1 to 10 dilution. The vial containing the diluted extract is labeled accordingly. If the original extract is 25mL the diluted extract vial will be labeled "250X".

12.7.4. Perform the dilution using an appropriate class A disposable volumetric pipette to transfer the extract and for the make-up volume of hexane. Ensure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

12.7.5. Transfer 1mL of the extract to a labeled 1.5mL GC autosampler vial. Record the sample data and submit with the sample extracts to the GC analyst.

13. Quality Control

13.1. The extraction technician should have completed an acceptable demonstration of capability before performing the method without supervision. The addition of spiking material to a sample or blank must be witnessed by another extraction technician and recorded in LIMS. All surrogates and matrix spikes must meet acceptable quality control limits.

13.2. A method blank sample and lab control spike must be prepared per each extraction batch or 1 per 20 samples, whichever is more frequent. A matrix spike/matrix spike duplicate (or lab duplicate) should be prepared per every extraction batch or 20 samples, whichever is more frequent or as per client specified quality assurance project plan (QAPP). If there is insufficient volume for a matrix spike/matrix spike duplicate, a note must be made in the comments section of the prep batch.

13.3. Default Spike for solid samples is 1.0mL of A1242 at 12.5ug/mL in acetone. Client and/or project specifications may dictate alternate amount or Aroclor.

13.4. PCB Surrogates TCMX and DCBP are added to each sample prior to extraction to measure extraction recovery. Default Surrogate for solid samples is 0.5mL of 0.5ug/mL TCMX/5.0ug/mL DCBP in acetone. Client and/or project specifications may dictate an alternate amount.

13.5. Also please see determinative method SOPs (S-NY-O-148 and S-NY-O-314 current revisions) for details

14. Data Analysis and Calculations

14.1. See determinative method SOPs (S-NY-O-148 and S-NY-O-314 current revisions) for details.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See determinative method SOPs for details.

16. Corrective Actions for Out-of-Control Data

16.1. See determinative method SOPs for details.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See determinative method SOPs for details.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. See determinative method SOPs for details.

19. Method Modifications

19.1. EPA Method 3546 uses a 1:1 Hexane:Acetone extraction solvent. The lab has found that a 1:1 ratio leads to the solvent boiling off and samples going dry during the extraction; therefore, the lab uses a 3:1 Hexane:Acetone extraction solvent.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. The technician should have received in-house safety training and should know the location of first-aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses, a lab coat, and nitrile gloves must be worn when handling glassware and samples.

22.2. The technician must review the Safety Data Sheets (SDS) for PCBs and all reagents used in the procedure before handling them. All solvents should be handled within a lab fume hood.

22.3. Microwave vessels, glass vials, and all other equipment should be examined prior to use for any defects that may cause a safety concern.

23. Waste Management

23.1. All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

23.2. Please refer to standard operating procedures in SOP S-NY-W-054 regarding how hazardous waste is handled and disposed of by the laboratory.

24. Pollution Prevention

24.1. Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used. Pace Analytical Services, Inc. employs extraction procedures such as micro-scale solvent extraction to reduce solvent requirements for solid extraction protocols.

24.2. Pollution prevention also relies on minimizing, to the best extent, the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP S-NY-S-168.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. U.S.EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

25.5. U.S. EPA Method 3546 Microwave Extraction, Revision 0, February 2007.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Spiking Concentrations for GEHR method sediment samples.

26.2. Attachment II: Microwave Extraction Conditions for PCBs in solid matrices.

27. Revisions

Document Number	Reason for Change	Date
S-NY-O-280-rev.04	General: converted to new format. General: removed procedure and calculation for determination of total solids and referenced applicable SOP Section 10: removed materials for cleanup methods. Section 12.6: removed cleanup methods and added reference to separate cleanup SOPs. Sections 25.1-25.3: added standard Pace references. Sections 25.5: Added	12Feb2015
S-NY-O-280-rev.05	Section 19.1: Added solvent ratio modification documentation	30March2015
S-NY-O-280-rev.06	General: updated SOP references Section 12.1.3: added requirement to document removal of foreign material or decanting of water Section 12.2.2: added additional detail Section 12.2.14 and Attachment II: added Microwave method used Sections 15.1 and 18.2: removed corrective actions and method performance criteria and referred to determinative method SOPs.	11June2015
S-NY-O-280-rev.07	General: updated definitions to match QAM Section 9: removed centrifuge and added PowerVap Section 12.2.5: added detail on when to reshape cell cap Section 12.2.9: removed use of pre-insertion tool Section 12.2.11.1: added documentation to face cell vents away from other cell vents Section 12.3: Added detail for how to set up the filtration system Section 12.3.9: added requirement to rinse the outside of the glass cell Section 12.5: added use of the PowerVap	02Feb2016

Attachment I: Spiking Concentrations for GEHR method sediment samples

Spiking Concentration for GEHR Sediment Samples

Laboratory Control Sample (LCS):

A quality control reference check standard (LCS) is also prepared and analyzed for Aroclor-1221 and Aroclor-1242 at a 3:1 ratio and a Total PCB concentration of 400ng/mL (300ng/mL Aroclor-1221 and 100ng/mL Aroclor-1242) in the extract. For sediment/solid samples, sodium sulfate is used for the quality control reference check standard (LCS). Calculate the percent recovery for the Aroclor spike and compare to the project limits of 50-150%. If the percent recovery for either Aroclor in the quality control reference check standard (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be re-extracted and re-analyzed (Exception: If the LCS recovery is high and there were no associated positive results for any Aroclor, then address the issue in the Case Narrative and no further action is needed).

Surrogate Compounds:

Surrogate compounds are added to each sample, performance evaluation (PE) sample, method blank, and quality control reference check standard (LCS) at time of extraction. The surrogate compounds TCMX and DCB are to be added for final extract concentrations of 10ng/mL and 100ng/mL, respectively.

Attachment II: Microwave Extraction Conditions for PCBs in solid matrices

Microwave Extraction Conditions for PCBs in Solid Matrices
Instrument Method Number: pcb_115C

Step	Time (minutes)	Watts	Temperature
1	13:00	1200	Ramp to 115°C
2	20:00	1200	Hold at 115°C

STANDARD OPERATING PROCEDURE

DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBS) AROCLORS

Reference Methods: EPA Method 8082A

SOP Number:	S-NY-O-314-rev.04
Effective Date:	02/06/16
Supersedes:	S-NY-O-314-rev.03

APPROVALS

Assistant General Manager	02/06/16 Date
Quality Manager	02/06/16 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
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1. Purpose/Identification of Method

1.1. This Standard Operating Procedure (SOP) is used to determine Polychlorinated Biphenyl (PCB) Aroclors by gas chromatography with electron capture detection and total Aroclor quantification using EPA SW-846 Method 8082A- Polychlorinated Biphenyl (PCB) Aroclors by capillary column gas chromatography (GC).

2. Summary of Method

2.1. Samples are extracted with a pesticide analytical grade solvent. The extracts are further processed by concentration and a series of clean-up procedures. The sample extracts are then analyzed by injecting onto a gas chromatographic system equipped with an electron capture detector.

2.2. The purpose of this SOP is to provide a detailed written document for quantification of PCBs as Aroclors according to SW-846 Method 8082A specification.

2.3. This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs as Aroclors by gas chromatography. Sample extraction and cleanup procedures are described separately in additional laboratory Standard Operating Procedures.

2.4. Extensive knowledge of this SOP and EPA Method 8082A is required. The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analysis of PCBs by Method 8082A.

3.2. **Parameters**: The following PCB Aroclors can be determined by this method:

Compound	CAS Number
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1262	37324-23-5
Aroclor 1268	11100-14-4

4. Applicable Matrices

4.1. This SOP is applicable in the determination and quantification of PCBs as Aroclors as outlined in EPA SW-846 Method 8082A. It is applicable to the following matrices: water, soil, sediment, sludge, oil, waste solvent, fish, tissue samples.

5. Limits of Detection and Quantitation

5.1. The following are default reporting limits as of the effective date of this SOP, and are subject to change without update to this SOP. Current reporting limits are on file with the QA Department and can be obtained by request.

Matrix	Sample Mass/Volume Extracted	Calibration Curve Low Standard	Extract Volume	RL (PQL) (all Aroclors)
Soil/Sediment Solid	10g	20ng/mL	25mL	0.050mg/kg
Soil/Sediment Solid	10g	20ng/mL	10mL	0.02mg/kg
Water	1 Liter	5ng/mL	10mL	0.050ug/L
Water	1 Liter	5ng/mL	5mL	0.025ug/L
Biota	10g (wet weight basis)	20ng/mL	25mL	0.050mg/kg
Waste Oil	0.5g	20ng/mL	25mL	1.00mg/kg
Wipe	1 Wipe	20ng/mL	25mL	0.500ug/wipe

5.2. Global MDL values can be obtained by request from the QA Department.

6. Interferences

6.1. Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Laboratory method blanks must be thoroughly reviewed for presence of non-target peaks and comparison of samples with blank chromatographic patterns.

6.2. Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

6.3. Polychloroterphenyls (PCTs), polybrominatedbiphenyls (PBB), polychlorinated naphthalenes (PCN), as well as dioxins can co-elute with PCBs. Carry-over from these compounds, when in high concentration, is common if clean-up procedures are not followed. These materials may be removed through the use of specified clean-up procedures.

6.4. Pesticides can be a source of contamination through breakdown into components such as hexachlorobenzene (HCB). This chlorinated compound can carry-over on the GC column, and contaminate samples. Specified clean-up procedures should be followed to eliminate this as a source of contamination when analyzing PCBs. High concentrations of pesticides can cause carry-over on GC columns.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Sample Collection and Preservation:

7.1.1. Routine soil, sediment, sludge, solid, caulk, and concentrated liquid samples should be collected in 8 oz clear glass wide-mouth jars, fitted with a Teflon-lined cap. Aqueous samples should be collected in 1 liter amber glass bottles with a Teflon-lined cap. Project specific protocols may require that containers be pre-cleaned to EPA specification protocol A –. Protect samples from light.

7.1.2. All samples must be placed on ice or refrigerated at >0-6°C from the time they are collected until delivery to the lab. Samples that are collected within driving distance of the laboratory and delivered the same day may not have reached temperature acceptance limits. These samples are deemed acceptable if evidence of cooling is present (i.e., they are received with ice in the cooler).

7.2. Sample Shipment:

7.2.1. Sample Shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

7.3. Sample Storage:

7.3.1. The samples must be protected from light and refrigerated at >0-6°C from time of receipt until they are removed from storage for extraction. Remaining sample material will be stored protected from light and refrigerated at >0-6°C. Sample will be disposed of or stored / archived according to project specifications.

7.3.2. Routine soil, sediment, sludge, solid, liquid and concentrated liquid samples are stored in a refrigerator dedicated for this type of sample.

7.4. Sample Extract Storage:

7.4.1. Sample extracts must be protected from light and refrigerated at >0-6°C. Sample extracts can be discarded after 45 days from issuance of final deliverables or can be archived in a freezer at less than -10°C for longer periods of time depending on the program requirements.

7.4.2. Field samples, sample extracts, and calibration standards must be stored separately.

7.5. Required Hold Time:

7.5.1. Extraction of solid samples by appropriate technique must be completed within one year from sample collection. Extraction of aqueous samples by appropriate technique must be completed within one year from sample collection. Sample extracts must be analyzed within forty days from extraction.

8. **Definitions**

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

8.2. Accuracy – The nearness of a result or the mean of a set to the true value. Accuracy is assessed by analysis of references samples and percent recoveries.

8.3. Analytical Batch –The basic unit for analytical quality control is the analytical batch, which is defined as samples which are analyzed together with the sample method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar matrices (e.g. water, sediment, soil, etc.).

8.4. Blank – A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix, however, a universal blank matrix does not exist for solid samples, but sometimes sodium sulfate is used as a blank matrix. The blank is taken through the appropriate steps of the process. A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field is sealed containers and transported back to the laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

8.5. Continuing Calibration Check Standard (CCCS) –The continuing calibration check standard contains all target analytes found in the calibration standards and is used to verify that the initial calibration is prepared correctly and that the instrument system is correctly calibrated. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

8.6. Calibration Standard (ICAL)– A series of known standard solutions used by the analyst for instrument calibration. Calibration standards are prepared from primary standard and/or stock standard solutions.

8.7. CAS Number – An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012, Columbus, OH 43210: [614] 447-3600).

8.8. Duplicate– A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

8.9. Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination as requested or required.

8.10. Initial Calibration – The process of analyzing standards, prepared at specified concentrations, to define the quantitative response relationship of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a calibration verification standard do not conform to the requirements of the method in use or at a frequency specified in the method..

8.11. Laboratory Control Sample (LCS) – A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to evaluate the performance of all or a portion of the measurement system.

8.12. Laboratory Control Sample Duplicate (LCSD) – A replicate laboratory control sample prepared and analyzed to obtain a measure of the precision of the recovery for each analyte.

8.13. Laboratory Method Blank – A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses..

8.14. Matrix – The predominant material of which the sample to be analyzed is composed; the substrate of a test sample. Matrix is not synonymous with phase (liquid or solid).

8.15. Matrix Spike – A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of sample for which an independent test result of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency..

8.16. Matrix Spike Duplicate – A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

8.17. Method Detection Limit (MDL) – The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

8.18. SDS – Safety Data Sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs.

8.19. PCB- Polychlorinated biphenyls are a class of 209 individual chemical compounds (congeners), in which one to ten chlorine atoms are attached to biphenyl. Use of PCBs has made them a frequent environmental pollutant.

8.20. Precision – The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. Precision is assessed by means of duplicate/replicate sample analysis.

8.21. Practical Quantitation Limit (PQL) - Another term for a method reporting limit. The lowest reportable concentration of a compound based on parameters set up in an analytical method and the laboratory's ability to reproduce those conditions

8.22. Quality Control – The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality; also the system of activities and checks used to ensure that measurement systems are maintained within prescribed limits, providing protection against "out of control" conditions and ensuring that the results are of acceptable quality.

8.23. Stock Solution – A concentrated reference solution containing one or more analytes prepared in the laboratory using an assayed reference compound or purchased from a reputable commercial source.

8.24. Surrogate – A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Pace Analytical Services, Inc. will use a Varian/Bruker Models 3800 and 450 (or equivalent) gas chromatograph (or equivalent), equipped with a Model 1177 split/splitless injector (or equivalent), temperature programmable oven, LEAP GC pal automatic sampler (or equivalent), and electron capture detector (or equivalent). A data system and integration of detector signal is interfaced to the gas chromatograph.

9.2. Chromatographic Data System: A data system for measuring peak height and peak area. An Empower computer network based workstation (Waters Corporation), will be employed to capture detector response and digitally store the chromatographic, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities..

9.3. Column (Primary Hydrogen Carrier Gas): ZB-1MS, Phenomenex Cat. No 7FD-G011-08; 20m x 0.18mm x 0.18um.

9.4. Column (Secondary Hydrogen Carrier Gas): ZB-5, Phenomenex Cat. No 7FD-G002-08; 20m x 0.18mm x 0.18um.

9.5. Hamilton Gastight syringes: 0.010 – 2.50mL

9.6. Class A pipettes: 1.00 – 100.0mL

9.7. Class A volumetric flasks: 5.00 100.0mL.

9.8. 8 dram vials and 4 vials dram for sample extract storage.

9.9. Pasteur pipettes.

9.10. 250mL and 100mL beakers, glass.

9.11. Disposable 1.0, 5.0, and 10.0mL pipettes.

9.12. Hexane, Burdick and Jackson-Pest Grade (or equivalent).

9.13. Acetone, Burdick and Jackson.-Pest Grade (or equivalent).

9.14. Toluene, Baker, (Cat.No. 9336-03) (or equivalent).

9.15. Methylene Chloride, Burdick and Jackson (Cat. No. 300-4) (or equivalent).

9.16. Ferrules: 0.4mm graphite/vespel, Restek 20229, and ¼" graphite ferrules, Restek 20210 or equivalent.

9.17. Injector septa: Thermolite Septa, Restek 20365 or equivalent.

9.18. Injector liner: Low Pressure Drop Liner w/Glass Wool, Restek 21033 or equivalent.

9.19. SGE Injector Syringe 10.0µL: SGE 002987 or equivalent.

9.20. Auto sampler vials: Snap vial 12x32mm Clear w/P, Microliter 11-5200 (or equivalent).

9.21. Snap Caps: 11mm Natural Snap Cap PTFE, Microliter 11-0051N-B (or equivalent).

10. Reagents and Standards

10.1. Aroclor Stock Standard Solutions:

10.1.1. Polychlorinated Biphenyls - Stock standards are prepared from individual Aroclor stock solutions from Accustandard. See Attachment 1 Table 1 for the exact preparation of each compound. Purchased stock standards should be stored according to manufacturer recommendations.

10.1.2. The stock standards are transferred into screw-cap boston bottles and stored under refrigeration at >0-6°C protected from light. Stock standards should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards. Stock PCB standards must be replaced after one year or sooner if a problem with instrument calibration is detected.

PCB Formulation	Supplier	Catalog # (or equivalent)	Conc. (PPM)
A1016	Accustandard	C-216S-H-100x	10000.0
A1221	Accustandard	C-221S-H-100x	10000.0
A1232	Accustandard	C-232S-H-100x	10000.0
A1242	Accustandard	C-242S-H-100x	10000.0
A1248	Accustandard	C-248S-H-100x	10000.0
A1254	Accustandard	C-254S-H-100x	10000.0
A1260	Accustandard	C-260S-H-100x	10000.0

A1262	Accustandard	C-262S-H-10x	1000.0
A1268	Accustandard	C-268S-H-10x	1000.0
TCMX/DCBP (surrogate)	Ultra Scientific	CUS-4911	500/5000

*unless otherwise noted Acetone is the solution used to make all stock standards.

10.2. Calibration Standards:

10.2.1. Calibration standards are prepared at five concentration levels using a prepared working standard. See Attachment I, Table 2 and for the preparation and exact concentrations of the working standards. The following five standards make up the initial calibration curve standard set for a High Level curve: 20ng/mL, 100ng/mL, 250ng/mL, 500ng/mL, 1000ng/mL. The following five standards make up the initial calibration curve set for a Low Level curve: 5ng/mL, 10ng/mL, 20ng/mL, 50ng/mL, 100ng/mL.

10.2.2. The two surrogates Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) are included in the A1254 calibration standards. The standard for TCMX/DCBP is prepared by diluting 1mL of TCMX/DCBP custom standard solution (ULTRA, cat.#CUS-4911, at 500/5000 ng/mL) into a 1000mL volumetric flask resulting in a solution of TCMX/DCBP at 0.5/5.0ug/mL.

10.2.3. Refer to Attachment I, Table 3 for instructions on preparation of the calibration standards containing A1254 and the surrogates. Refer to Attachment 1, Table 2 for instructions on preparing the remaining calibration standards.

10.2.4. Transfer all calibration standards to ASE vials and store in a refrigerator at >0-6°C, protected from light. Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

10.3. PCB Continuing Calibration Stock Standards:

10.3.1. The stock standards are transferred into a screw cap boston bottles and stored in a refrigerator protected from light. Stock standard should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards. Stock PCB standards must be replaced annually or sooner if a problem with instrument calibration is detected.

PCB	**Supplier**	**Catalog # (or equivalent)**	**Conc. (ug/mL)**
A1016	Chem Service	S-11086J	1000
A1221	Chem Service	S-11087J	1000
A1232	Chem Service	S-11088J	1000
A1242	Chem Service	S-11089J	1000
A1248	Chem Service	S-11090J	1000
A1254	Chem Service	S-11091J	1000

A1260	Chem Service	S-11092J	1000
A1262	Ultra Scientific	EPA-1372	1000
A1268	Ultra Scientific	EPA-1382	1000

10.4. Continuing Calibration Standards:

10.4.1. The surrogate compounds Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) are included in all Continuing Calibration Check Standards at a concentration near the mid-point of the surrogate calibration curve sequence. All continuing calibration standards are prepared independently from calibration standards, by using an alternate source purchased from standard vendors. Refer to Attachment II, Tables 1-3 for instructions on preparation of these standards.

10.5. Surrogated Instrument Blank Solution: A surrogated instrument blank standard is analyzed after each CCCS to check for instrument carry over. The surrogated instrument blank is prepared as follows:

10.5.1. High Level Instrument Blank: 2.0mL of the 0.5/5.0PPM TCMX/DCBP solution is diluted to 100mL in a volumetric flask set to volume in hexane. This results in a 10/100PPB TCMX/DCBP solution.

10.5.2. Low Level Instrument Blank: 1.0mL of the 0.5/5.0PPM TCMX/DCBP solution is diluted to 100mL in a volumetric flask set to volume in hexane. This results in a 5/50PPB TCMX/DCBP solution.

11. Calibration and Standardization

11.1. Gas chromatographic operation parameters: See Attachment III.

11.2. Retention Times:

11.2.1. The retention time (RT) windows are established from the continuing calibration check standard (CCCS) peak retention times. The CCCS is analyzed three times over a 72-hour period and the standard deviation is calculated from the three retention time measurements. The standard deviation is multiplied by three and this establishes the retention time window for each quantified peak (±3SD). Use the retention time for a peak in the continuing calibration check standard to determine the midpoint of the retention time window for the analysis sequence. If the continuing calibration checks fall outside of these windows update the windows using the previous check standard. If the retention times are still outside the established windows instrument maintenance must be performed and recalibration may be required.

11.2.2. This function is performed in the chromatography software graphically as vertical dropdown retention time markers with retention time window brackets. Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-response sample analysis.

11.3. Retention time studies are performed for each instrument annually and are available upon request form the QA department

11.4. Initial GC Calibration:

11.4.1. GC calibration is performed by the external standard calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

11.4.2. Establish the gas chromatographic operating parameters outlined in the Procedure section and prepare the calibration standards at the five concentrations outlined in the Reagent and Standard section. Inject each calibration standard using the GC Autosampler and the parameters outlined in the Procedure section. Note: The same parameters are used for actual samples.

11.4.3. For each Aroclor, 5 peaks are selected to prepare calibration curves. The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (i.e., minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with organochlorine pesticides. The determined area of the five peaks selected for calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and the peak numbers used.

Aroclor	**Peak Numbers**
A1016	6, 7, 8, 9, 10
A1221	1, 2, 3, 4, 5
A1232	5, 7, 8, 9, 10
A1242	6, 7, 8, 9, 10
A1248	11, 12, 13, 14, 15
A1254	16, 17, 18, 19, 20
A1260	20, 21, 22, 23, 24
A1262	20, 21, 22, 23, 24
A1268	23, 24, 25, 26, 27

11.4.4. For the initial calibration curve to be considered valid, the percent relative standard deviation of response factors must be less than 20% over the working range if average calibration factor quantitation is used. Note: the % RSD is a useful check for linearity through the origin and is used as a data quality indicator. In general an inverse weighted linear calibration curve with intercept is used for quantitation and is not replaced with the average calibration factor. For linear calibration curve the Correlation Coefficient R must be greater than 0.995.

11.4.5. Once linear calibration has been established it is subjected to an additional check. This check is the comparison of the calculated amount of the low calibration standard for each Aroclor against the expected amount of the standard using the % difference. Re-fitting the calibration data back to the model or calculating the % difference is determined by using the following equation:

% Difference = (Cc-Ce/Ce)x100

Where Cc=Calculated amount of standard, in mass or concentration units.

Ce=Expected amount of standard, in mass or concentration units.

The absolute value of the percent difference between these two amounts for

Every calibration level should be less than or equal to 20%.

11.4.6. Our laboratory uses a computer based chromatography software module (Water Corporation, Empower software) interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. Integration of peak areas and production of chromatograms is performed in the Empower software. All data analysis will be carried out in Empower including calculating calibration curves/response factors, report generation, and archival of data.

11.4.7. If a re-calibration is performed, the CCCS must be analyzed again and values calculated using the new relative response factors. If the CCCS fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.*, GC gas leak, autosampler syringe plugged, broken injector liner).

11.5. Retention Time Windows:

11.5.1. The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Select a calibration standard and inject three times over a 72-hour time period.

11.5.2. For each peak calculate the standard deviation resulting from the variation in the three retention times for that peak.

11.5.3. The retention time window is defined as plus or minus three times the standard deviation of the three retention time determinations.

11.5.4. If the standard deviation of the selected peak is zero, then a default standard deviation of 0.01 minutes is used. If it is the last eluting peak that the zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

12. **Procedure**

12.1. Sample Extraction and Preparation may be performed by a variety of approved extraction methods employed by the laboratory. These methods may include but are not limited to EPA Methods 3546, 3540C, 3545A, 3580A, 3535A, 3510C, and 3520C. See separate extraction SOPs for details.

12.2. Gas Chromatographic Procedures:

12.2.1. Prescreening of sample extracts: Prescreening is a fast and effective way to determine if re-extracts or dilutions for over ranged samples are required. See SOP S-NY-O-140 PCB Screening, current revision for details.

12.2.2. Approximately 1.0mL of the final dilution extract is then transferred into a labeled autosampler vial.

12.2.3. The sequence of the analytical queue is set up in the Laboratory Information Management System (LIMS) as a unique batch file. This file contains the exact order in which standards, instrument blanks, and samples will be analyzed.

12.2.3.1. Analytical Sequence Queue: The following is an example of the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run after every 10 samples in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples. Below is an example of an analytical sequence.

Order of Material Injected
Hexane Blank
Initial Calibration Standards
Hexane Blank
Continuing Calibration Check Standard
Hexane Blank w/surrogates
Samples, including method blanks, matrix spikes, matrix duplicates, matrix spike duplicates, and QC reference

check standard. A maximum of ten samples between continuing calibration check standards
Continuing calibration check standard
Hexane Blank w/surrogates

12.2.4. Once the sample set is uploaded into the Empower acquisition/run screen and saved, the sample set is printed and the samples are loaded into the GC autosampler tray in the order specified by the sample set queue.

12.2.5. The following labeling will be used on the autosampler vial and for the sample set file created for the analytical queue.

12.2.4.1. The initial calibration standard will be labeled as 040516A, 040516B, etc. Substitute the actual date of analysis and the Aroclor used in the file name.

12.2.4.2. The instrument blanks will be labeled 070405B01, B02, B03, etc. Substitute the actual date of analysis in the file name.

12.2.4.3. The continuing calibration check standards will be labeled CS160405A CS160405B, etc. Substitute the actual date of analysis and the Aroclor used in the file name.

12.2.4.4. Samples are labeled with the laboratory identification number on the autosampler vial. In the sample set file the laboratory identification number, along with the client identification, sample weight, set volume and dilution are entered.

12.2.6. At this point the chromatography software can be initiated to start data collection. The gas chromatograph is placed into run mode and sample analysis is performed until the analytical queue is complete.

12.2.7. Peak Identification:

12.2.7.1. Target peaks are identified in unknown samples based upon Retention Time (RT). The retention time of an unknown peak must fall within the retention time windows established.

12.2.7.2. Besides using retention time windows to assign peak IDs, the analyst should also rely on their own experience in recognition of multi-response PCB chromatograms. Caution should be exercised when identifying peaks which elute near interferences present in samples and blanks. Comparison of sample chromatograms with method blank and field blank chromatograms is useful in determining chromatographic interferences.

12.2.7.3. This method should be applied with caution when used in determining PCB of interest in unknown sample for which no prior historical information exists. In this case confirmatory column analysis or confirmation by GC/MS analysis may be advised.

12.2.8. PCB Aroclor Qualitative Identification and Secondary GC Column Confirmation:

12.2.8.1. Positive identification of PCB Aroclors is based on comparison of retention time of the five selected quantitation peaks and major non-quantitation peaks for the unknown sample with retention time of reference standards (continuing calibration check standards). Additionally pattern recognition is used for comparison of unknown samples with reference standards for positive identification.

12.2.8.2. In cases where multiple Aroclors are present with overlapping chromatographic patterns or interferences are encountered that are not removed with extract cleanup processes one or two quantitation peaks may be dropped and not used for quantitation. A minimum of 3 quantitation peaks

must be used for all unknown samples and standards. When quantitation peaks are dropped for a sample or standard the corresponding peaks are also dropped in the initial calibration sequence for calculation purposes.

12.2.8.3. Dual Column/Confirmatory Column Analysis by GC: Inject samples under same operating conditions and analytical run QA/QC parameters on a secondary GC column of dissimilar phase (e.g., ZB-1 and ZB-5). Note: If using dual GC column system, samples are injected sequentially through separate injection ports onto both columns. Samples are analyzed and concentration results are reported.

12.2.8.4. Dual Column/Confirmatory Column Laboratory Default by SW-846:

12.2.8.5. Report lowest concentration of the 2 column results for each individual Aroclor on the merged EDD, Form 1 or Certificate of Analysis (Note: This is appropriate for Aroclor regulated projects).

12.2.8.6. If RPD percent exceeds 40% report the lowest concentration result of the two analyses unless observed chromatographic interference or instrumental analysis QA/QC indicates the higher value may be more accurate. P-flag all excursions > 40% and describe interferences or rationale for reporting lower value in Data Narrative.

12.2.8.7. If a concentration is above the PQL on one column and below the PQL on the second column, the qualitative presence is not confirmed and the sample is reported as not detected. Note: If reporting to the MDL is required do the following: For reporting to the MDL: a) If one result is greater than the PQL and other result is < PQL (J-flag) Report the highest result as confirmed (*unless interference or QC reasons indicate lower value*); b) If one result is above MDL (J-Flag) and second is Not Detected report the concentration as not detected. (Presence not confirmed); c) If both results are J-Flag values (< PQL) report the lowest value of the two.

12.2.9.

12.3. Data Reduction/Reporting:

12.3.1. Final peak assignments and quantitation calculations are performed within the software along with the current instrument calibration. The final concentration results are provided in the reporting section of the software..

12.3.2. A-note/P-note: Aroclor qualifier notes are used on a per client basis to provide additional information regarding chromatographic observations such as environmental alteration of an Aroclor (A-note) or existence of an Aroclor with non-quanitified peaks or a similar pattern (P-note).

12.3.3. Data Qualifiers: Sample Concentration Reports (Certificates of Analysis, Data Package Form 1's and Electronic Data Deliverables (EDDs) are generated using the appropriate data qualifiers as defined in Laboratory Form F-NY-Q-033 "Report Definitions Page" current revision.

13. Quality Control

13.1. The table below outlines the data assessment, acceptance criteria, and corrective action procedures for non-compliant data.

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action

Initial Calibration	The five point calibration is analyzed initially for all Aroclors and when Continuing Calibration Check standard fail criteria.	- %RSD≤20% for the relative response factors for the calibration standards if using average response factor calibration. Correlation Coefficient R must be >0.995 for Linear Regression.	- Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria.
Continuing Calibration Check Standard (CCCS)	- Initially analyze a CCCS immediately following an initial calibration. - After the initial CCCS of the sequence, a CCCS must be analyzed after 10 samples. - Analytical sequence must end with analysis of a CCCS. - CCCS must be analyzed at least once per 12 hour analytical shift. - CCCSs are rotated through all Aroclors.	- Calibration factor for the continuing calibration check must ±20% of the true value. - Retention time of all quantitated peaks must be within RT window (reset with each initial CCCS of a sequence). - All samples must be bracketed by CCCS that meet all criteria stated above.	- If the reason for the failure of the CCCS appears to be a poor injection (or a degraded standard solution), the CCCS will be re-injected (or re-prepared and re-injected) immediately following the failed CCCS. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCCS meets all the acceptance criteria and there is no apparent impact on the sample data the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. - If CCCS failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCCS failure, correct system, and recalibrate if necessary. Initial calibration and CCCS criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCSs must be reanalyzed. -If acceptable CCCSs are observed later in the sequence, samples

			bracketed by acceptable CCCSs will be reported. Samples between the failed CCCS and prior/ subsequent complaint CCCS will be re-analyzed. - Exception: Samples that are non-detect for analytes of interest may be reported with a high bias if a bracketing CCCS fails high.
-Retention Time (RT)	- RT windows are established annually. - Use the retention time for peaks in the CCCSs to determine midpoint of the relative retention time window for the analysis sequence. -Each sample analysis: Rely on RT windows to identify PCB Aroclor to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because compound composition may shift RT for GC peaks.	- Each quantitated peak and surrogate peak should be within established windows.	-Inspect chromatographic system for malfunction, correct problem. Perform re-analysis or re-calibration if necessary.
Method Blank	-One per extraction batch of ≤20 samples of the same matrix per day. -Should be analyzed with other associated batch QC samples on the same instrument, but not all samples. -Must undergo all sample preparative procedures.	- Concentration does not exceed the RL/MDL for any PCB Aroclor. - Must meet in house surrogate criteria*	- Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. -If method blank is found to contain PCB contamination above the RL/MDL for any PCB Aroclor compound, then re-extract and re-analyze all associated

			samples. -If no sample is available for re-extraction, report data with a B-flag to indicate method blank contamination.
Laboratory Control Spike (LCS)	- One per extraction batch of ≤20 samples per matrix per day. - Should be analyzed with other associated batch QC samples on the same instrument, but not all samples.	-Percent recovery must be within method limits of 70-130%. - Must meet in house surrogate criteria*	-Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. -If LCS recovery is still out of limits, then re-extract and re-analyze all associated samples. -If no sample is available for re-extraction, report data flagged to indicate LCS failed recovery.
Laboratory Control Sample Duplicate (LCSD)	- One per extraction batch of ≤20 wipe samples per day. - Should be analyzed with other associated batch QC samples on the same instrument, but not all samples.	-Percent recovery must be within method limits of 70-130%. - Relative percent difference (RPD) should be within 20% - Must meet in house surrogate criteria*	-Re-analyze LCSD to determine if instrument was the cause. If LCSD passes, then report samples. -If LCSD recovery is still out of limits, the re-extract and re-analyze all associated samples. -If no sample is available for re-extraction, report data flagged to indicate LCSD failed recovery.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	-One MS/MSD per extraction batch of ≤20 samples of similar matrix. - An MS/DUP may be appropriate in place of MS/MSD in matrices	-Relative percent difference (RPD) should be within 30%. - Must meet in-house Aroclor spike recovery criteria*	-Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. -Check for errors such as calculations and spike

	where detectable amounts of analytes are known to be present.	- Must meet in house surrogate criteria* (unless parent sample is also outside of criteria)	preparation. -Check parent sample results and surrogate recovery for indications of matrix effects. -If no errors are found, and the associated LCS is within limits, then sample matrix effects are likely the cause. Note exceedance in case narrative.
Sample Duplicate (DUP)	- When used in place of an MS/MSD: One MS/DUP per extraction batch of ≤20 samples of similar matrix.	-Relative percent difference (RPD) should be within 30%. - Must meet in house surrogate criteria* (unless parent sample is also outside of criteria)	- Re-analyze the sample and sample duplicate to determine if the instrument was the cause. If RPD is within limits in re-analysis, then report the data. - Check surrogate recovery for indications of matrix effects. - Check for calculation errors. - If no errors are found, and the associated LCS is within limits, than sample matrix effects are likely the cause. Note exceedance in the case narrative.
Surrogates	-Calibrated as target compound in the Aroclor A1254 standards. -Surrogates are added to all calibration check standards, blanks (including instrument blanks run after CCCS), samples and QC samples.	- Must meet in house surrogate criteria*	-Re-analyze the affected sample or QC sample to determine if instrument was the cause. If surrogate passes, then report samples. -Check for errors in surrogate calculation and surrogate solutions. -If no problem is found, then re-extract and re-analyze the sample. -If re-extraction is within limits and sample extract holding time, then report only the re-analysis.

			-If the re-extraction is within limits, but out of extraction holding time, then report both sets of data. -If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. -If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have a client re-sample.

***Note:** In-house recovery limits are established annually for surrogates and matrix spike/matrix spike duplicate samples. Current recovery limits are on file with the QA department.

14. Data Analysis and Calculations

14.1. Percent Recovery

P = A-B/T x 100

P = Percent recovery, %
A = concentration of analyte (PCB) in the spike sample aliquot
T = Know true values of the spike concentration
B = Background concentration of analyte (PCB) in the unspiked sample aliquot

14.2. RPD (Relative Percent Difference)

RPD = (DUP1-DUP2)/AVG x 100

RPD = Relative Percent Difference
DUP1 = The greater of the measured values
DUP2 = The lesser of the measured values
AVG = Average of the two analyses

14.3. PCB Solution concentration calculation from initial Calibration by Linear Regression:

Yi= aXi + b

Xi = Calibrated Solution Concentration (ng/mL)
Yi = total area response of 5 PCB quant. peaks (uV-Sec.)
a = slope
b = intercept

Note: In those instances where samples may be quantitated with 3-4 peaks due to interference or overlap, the Empower system automatically quantitates against the calibration using only the area of the selected peaks.

Unknown Solution Conc. X = (Y –b) a

Y = Total area response of PCB Chromatogram (uV-Sec.)
a = slope of ICAL by linear regression
b = intercept of ICAL by linear regression

14.4. Capillary GC: Sample calculations:

14.4.1. The concentration of each identified PCB Aroclor in a sample will be calculated based on the sample weight or volume.

14.4.2. The PCB solution concentration of the extract is calculated as follows:

Solution Conc. = (Y –b)/a

Y = Total area response of PCB Chromatogram (uV-Sec.)
a = slope of ICAL by linear regression
b = intercept of ICAL by linear regression

14.5. Final concentration of samples- Calculations of final PCB concentrations will vary upon matrix, calculations are as follows:

14.5.1. Soil/Sediment/Solids:

Final Conc. = (Sol. Conc.) * (V)*DF/ (M)* (%Total Solids) (1/1000) ug/g

Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

14.5.2. Water:

Final Conc.= (Sol. Conc.) * V*DF/[(Vt)](1/1000) ug/L

Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
Vt= Total Volume Extraction (L)

14.5.3. Biota Tissue :

Final Conc. = (Sol. Conc.) * (V)*DF/(M)(1/1000) ug/g

Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

14.5.4. Waste Oil:

Final Conc. = (Sol. Conc.) * (V)*DF/ (M)*(%Total Solids) (1/1000) ug/g

Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

14.6. The calculated concentration for each PCB Aroclor will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results with concentrations at or above the MDL but below RL will be reported as detects and flagged as estimated (J-flag). The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

15.2. Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

15.3. The analyst may also consult with the Quality Manager as to the best form of action to take or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a LabTrack Ticket (LTT) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This LTT is reviewed by the Quality Manager and lab management to verify that appropriate actions have been taken to correct the problem.

15.4. Please see Table 13.1 below for specific Quality Assurance Acceptance Criteria.

16. Corrective Actions for Out-of-Control Data

16.1. See table in section 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Data that is detected to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

17.1.1. If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operation condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

17.1.2. If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is control.

17.1.3. If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

17.1.4. In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a LabTrack Ticket will be issued to define the problem, steps to correct the problem, and final resolution.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study**: Method detection limits are established according to the method established in 40 CFR 136, Appendix B. See SOP S-NY-Q-021 Determination of LOD and LOQ current revision for details.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Training Procedures.

19. Method Modifications

19.1. SW-846 EPA Method 8082A specifies to use Aroclors 1016 and 1260 for matrix spike samples unless specified by the client. The laboratory uses Aroclor 1242 as the default spike analyte due to historic contamination in the area coming from this Aroclor.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Safety glasses and disposable gloves must be worn when handling samples and extracts.

22.2. All manipulations of sample extracts should be conducted inside a chemical fume hood. Manipulation of sample extracts outside of a fume hood should be minimized by the analyst.

22.3. Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with

the precautions for handling solvents and chemicals used to process samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

22.4. Samples remaining after analysis should either be returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance and also SOP S-NY-O-054, disposal of laboratory waste.

23. Waste Management

23.1. All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

23.2. Please refer to SOP S-NY-W-054 regarding how hazardous waste is handled and disposed of by the laboratory.

24. Pollution Prevention

24.1. Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Pace Analytical Services, Inc. employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols and ASE and Soxhlet extractions for solid matrices.

24.2. Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP S-NY-S-168.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. U.S. EPA SW-846 Method 8082A "Test Methods for Evaluating Solid waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

25.5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures of the Analysis of Pollutants", July, 1988.

25.6. New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1996.

25.7. Guide to Environmental Analytical Methods", third edition, Genium Publishing Corporation, 1997.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: PCB Stock Standard/Calibration Standard Preparation.

26.2. Attachment II: Continuing Calibration Check Standard Preparation.

26.3. Attachment III: GC Operating Parameters Example

26.4. Attachment IV: Chromatograms.

27. **Revisions**

Document Number	Reason for Change	Date
S-NY-O-314-rev.01	General: converted to new format. General: removed all references to air matrix (PUF). Sections 10.1-10.4: updated standards used and instructions for working standard creation Sections 11.2.5 and 13.6.2: added Section 12.1: revised to match current SOP list. Sections 13.6.3 and 16.1: updated surrogate recovery acceptance limits Section 16.1: specified that surrogate calibration is done with Aroclor 1254 Sections 25.1-25.3: added standard Pace references. Section 26.1: updated attachment	12Feb2015
S-NY-O-314-rev.02	Sections 13.10.2 and 14.1: added documentation regarding quantitation with 3-4 peaks	30March2015
S-NY-O-314-rev.03	Section 5.2: changed to reference 40 CFR MDL procedure Section 12.3.2: removed qualifiers and referred to Report Definitions Page controlled document form Sections 15.3 and 17.1.4: updated to reference LabTrack system Section 19.1: added documentation of modification for use of Aroclor 1242 as default spiking analyte	10June2015

	Section 5.1: added note that PQLs are subject to change Section 7.4.1: updated extract storage time to match QAM Section 8: updated definitions to match QAM Section 9: removed Helium columns and added syringes Section 10: updated standard storage temperatures Section 10.5: added Surrogated Instrument Blanks Section 11.1: moved Retention Time Window information from section 13 Sections 11.4.4 and 13.1: updated correlation coefficient value to >0.995 Section 12.1: removed table Section 12.2.1: removed screening procedure and referenced screening SOP Section 12.2.8: moved Peak Identification and confirmation procedures from section 13 Section 12.3: removed QA review of final results and added use of A/P-notes Section 13: moved table from 16.1 and updated to use of in-house limits Section 16: removed table and referenced section 13 Section 18: removed DOC and MDL specifications and referenced applicable SOPs Section 25: removed reference to Standard Methods Attachments III and IV: updated to current versions	
S-NY-O-314-rev.04		05Jan2016

Attachment I: PCB Stock Standard/Calibration Standard Preparation

Table 1: PCB Stock Standard Preparation Table

PCB Stock Standards	Init Volume (mL)	Final volume (mL)	Conc. (ppm)
A1016	5.0	50	10.0
A1221	5.0	50	10.0
A1232	5.0	50	10.0
A1242	5.0	50	10.0
A1248	5.0	50	10.0
A1254	5.0	50	10.0
A1260	5.0	50	10.0
A1262	1.0	100	10.0
A1268	1.0	100	10.0

Unless otherwise noted hexane is the solution used to make all dilutions. *Custom Order

Table 2: PCB Calibration Standard Preparation Table (High Level Calibration Curve)

Initial Volume (mL)	Initial Conc. (ug/mL)	Final Volume (mL)	Final Concentration (mg/L)							
			A1016	A1221	A1232	A1242	A1248	A1260	A1262	A1268
5.0	10.0	50.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2.5	10.0	50.0	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500
1.25	10.0	50.0	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250
0.500	10.0	50.0	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
5.0	1.00	50.0	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020

See Table 3 for A1254 Standard Preparation (high level)

Attachment I: PCB Stock Standard/Calibration Standard Preparation (continued)

Table 2A: PCB Calibration Standard Preparation Table (Low Level Calibration Curve)

Init. Volume (mL)	Initial Conc. (ug/ml)	Final Volume (mL)	Final Concentration (ppm)							
			A1016	A1221	A1232	A1242	A1248	A1260	A1262	A1268
0.5	10.0	50.0	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
2.5	1.0	50.0	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
1.0	1.0	50.0	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
1.0	0.500	50.0	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
0.50	0.500	50.0	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

See Table 3A for A1254 Standard Preparation (low level)

Table 3: PCB A1254 Calibration Standard Preparation Table (for High Level Curve)

Initial Volume (mL) A1254	Initial Conc. (ug/mL) A1254	Initial Volume (mL) 0.5/5.0 -ppm Surrogate	Final Volume (mL)	Final Concentration (ppm)		
				A1254	TCMX	DCBP
5.0	10.0	0	50	1.000	0	0
2.5	10.0	0	50	0.500	0	0
5.0	10.0	2.00	50	1.000	0.020	0.200
2.5	10.0	1.00	50	0.500	0.010	0.100
1.25	10.0	0.800	50	0.250	0.008	0.080
0.500	10.0	0.500	50	0.100	0.005	0.050
1.00*	1.00	0.200	50	0.020	0.002	0.020

*This initial volume is of the A1254 1.00ug/mL secondary stock solution WITHOUT surrogates

Attachment I: PCB Stock Standard/Calibration Standard Preparation (continued)

Table 3A: PCB A1254, TCMX and DCBP Calibration Standard Preparation Table (for Low Level Curve)

Initial Volume A1254 (mL)	Initial Conc. A1254 (ug/mL)	Initial Volume (mL) 0.5/5.0 -ppm Surrogate	Final Volume (mL)	Final Concentration (ppm)		
				A1254	TCMX	DCBP
0.5	10.0	0.800	50	0.100	0.00800	0.0800
2.50	1.000	0.500	50	0.050	0.00500	0.0500
1.0	1.000	0.400	50	0.020	0.00400	0.0400
1.0	0.500	0.250	50	0.010	0.00250	0.0250
0.50	0.500	0.100	50	0.005	0.00100	0.0100

Attachment II: Continuing Calibration Check Standard Preparation

Table 1: PCB Continuing Calibration Working Standards prepared from 1000ug/mL Stock Standards

PCB	Initial Volume (mL)	Final Volume (mL)	Concentration (ppm)
A1016	1.0	100	10.0
A1221	1.0	100	10.0
A1232	1.0	100	10.0
A1242	1.0	100	10.0
A1248	1.0	100	10.0
A1254	1.0	100	10.0
A1260	1.0	100	10.0
A1262	1.0	100	10.0
A1268	1.0	100	10.0

Table 2: PCB Continuing Calibration Standards (High Level) prepared from 10ug/mL CCV Working Standards and all contain surrogates

PCB	Surr. Volume* (mL)	Initial Volume Aroclor (mL)	Final Volume (mL)	Surrogate Concentration TCMX/DCBP (ppm)	Aroclor Concentration (ppm)
A1016	2.0	5.0	100	0.010/0.100	0.500
A1221	2.0	5.0	100	0.010/0.100	0.500
A1232	2.0	5.0	100	0.010/0.100	0.500
A1242	2.0	5.0	100	0.010/0.100	0.500
A1248	2.0	5.0	100	0.010/0.100	0.500
A1254	2.0	5.0	100	0.010/0.100	0.500
A1260	2.0	5.0	100	0.010/0.100	0.500
A1262	2.0	5.0	100	0.010/0.100	0.500
A1268	2.0	5.0	100	0.010/0.100	0.500

*Surrogate stock solution 0.500ug/mL TCMX and 5.0ug/mL DCBP

Attachment II: Continuing Calibration Check Standard Preparation (continued)

Table 3: PCB Continuing Calibration Standards (low Level) prepared from 10.0ug/mL CCV Working Standards and all contain surrogates.

PCB	Surr. Volume* (mL)	Initial Volume Aroclor (mL)	Final Volume (mL)	Surrogate Concentration TCMX/DCBP (ppm)	Aroclor Concentration (ppm)
A1016	1.0	0.500	100	0.005/0.050	0.050
A1221	1.0	0.500	100	0.005/0.050	0.050
A1232	1.0	0.500	100	0.005/0.050	0.050
A1242	1.0	0.500	100	0.005/0.050	0.050
A1248	1.0	0.500	100	0.005/0.050	0.050
A1254	1.0	0.500	100	0.005/0.050	0.050
A1260	1.0	0.500	100	0.005/0.050	0.050
A1262	1.0	0.500	100	0.005/0.050	0.050
A1268	1.0	0.500	100	0.005/0.050	0.050

*Surrogate stock solution 0.500ug/mL TCMX and 5.0ug/mL DCBP

Attachment III: Example GC Operating Parameters

GC #: GC-21 8082 High Level Method (GEHR inclusive, parameters)
Method: Method 2
Column: ZB-1 Front
ZB-5 Middle
Date: 01/18/2012
Analyst: JKA
File Name: S:\Lab Data\PCB\GC Parameters\[GC21_Parameters.xls]8082 M2

Sample Delivery: SEE LEAP PARAMETERS

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.5	30.5

Stabilization Time (min): 0.20

Injector: Front CP-1177

1177 Oven Power: ON
1177 Temperature (°C) 300

Time	Split State	Split Ratio
Initial	ON	30

Flow/PSI(Front EFC, Type 1):

Carrier Gas: Helium

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*30.0**	-------	20	20

Constant Flow Mode Enable: NO
Column Flow Rate (ml/min): 5.0

Injector: Middle CP-1177

1177 Oven Power: ON
1177 Temperature (°C) 300

Time	Split State	Split Ratio
Initial	ON	30

Flow/PSI(Front EFC, Type 1):

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*30.0**	-------	20	20

Constant Flow Mode Enable: NO
Column Flow Rate (ml/min): 5.0

Detector: **Front ECD** **Middle ECD**

	Front ECD	Middle ECD
ECD Oven Power:	ON	ON
Temperature (°C)	300	300
Electronics:	ON	ON
Range:	1	1

Time	Range	Autozero
Initial	1	YES

Time	Range	Autozero
Initial	1	YES

Front ECD Adjustment

Time Constant:	Fast	Fast
Cell Current:	CAP	CAP
Contact Potential (mV):	-650 *	-380 *
Date of last adjustment	12/15/2011	12/15/2011

Front ECD Adjustments
Make-up Flow (mL/min) 35 *

Middle ECD Adjustments
Make-up Flow (mL/min): 35 *

*values may change with use

Analog Output

Detectors:	Front: ECD	Attenuation	1
	Middle: ECD	Attenuation	1
	Rear: None		

Attachment III: Example GC Operating Parameters (continued)

GC-10 8082 High Level Method - Hydrogen

GC #:	**10**
Method:	**Hydrogen 8082**
GC Method #:	**2**
Date:	**02/09/2012**
Analyst:	**MTH**
File Name:	
Column:	**Front ZB-1 MS 20m 0.18 0.18**
	Middle ZB-5 20m 0.18 0.18

Sample Delivery: SEE LEAP PARAMETERS

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	150		1.41	1.41
	290	17.5	0.65	10.04

Stabilization Time (min): 0.5

Injector: Front CP-1177

1177 Oven Power: ON
1177 Temperature (°C) 300

Time	Split State	Split Ratio
Initial	ON	30

Flow/PSI(Front EFC, Type 1):

Carrier Gas Hydrogen

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*30 **		10.00	10.00

Constant Flow Mode Enable: NO
Column Flow Rate (ml/min): 5.0

Detector: **Front ECD**

ECD Oven Power: ON
Temperature (°C) 300
Electronics: ON
Range: 1

Time	Range	Autozero
Initial	1	YES

Front ECD Adjustment
Time Constant: Fast
Cell Current: CAP
Contact Potential (mV): 250 *
Date of last adjustment 01/23/2012
Make-Up Flow (ml/min): 35.0
*values may change with use

Analog Output

Detectors: Front: ECD Attenuation 1
Middle: ECD Attenuation 1
Rear: None

Injector: Middle CP-1177

1177 Oven Power: ON
1177 Temperature (°C) 300

Time	Split State	Split Ratio
Initial	ON	30

Flow/PSI(Front EFC, Type 1):

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*30 **		10.00	10.00

Constant Flow Mode Enable: NO
Column Flow Rate (ml/min): 5.0

Middle ECD

ECD Oven Power: **ON**
Temperature (°C) 300
Electronics: ON
Range:

Time	Range	Autozero
Initial	1	YES

Fast
CAP
365 *
01/23/2012
35.0

Attachment III: Example GC Operating Parameters (continued)

Leap GC Pal Parameters					
Sample injection Methods					
Method	**GC Dual**	**GC Duals**		**Method**	**GC Inj s**
Cylcle	GC Dual	GC Dual		**Cylcle**	GC Inj S
Syringe	10uL	10uL		**Syringe**	10uL
1. Sample Vol	1.0uL	1.0uL		**1. Sample Vol**	1.0uL
1. Air Vol	1.0uL	1.0uL		**Solvent Plug**	200nL
1. Inject to	GC Inj 1	GC Inj 1		**Slv Source**	Standard
Inj Time Diff	0s	0s		**Int Standard**	0nL
2. Sample Offs	1	0		**Std Source**	Standard
2. Sample Vol	1.0uL	1.0uL		**Air Gap (s)**	1.0uL
2. Air Vol	1.0uL	1.0uL		**1. Air Vol Ndl**	1.1uL
2. Inject to	GC Inj 2	GC Inj 2		**Pre Cln Slv 1**	2
Pre Cln Slv 1	2	2		**Pre Cln Slv 2**	2
Pre Cln Slv 2	2	2		**Fill Speed**	5.0uL/s
Pre Cln Sp 1	0	0		**Pull Up Delay**	1.0s
Int Cln Slv 1	2	2		**Inject to**	GC Inj 1
Int Cln Slv 2	2	2		**Inject Speed**	5.0uL/s
Pst Cln Slv 1	2	2		**Pre Inj Del**	0ms
Pst Cln Slv 2	2	2		**Pst Inj Del**	0ms
Fill Volume	10uL	10uL		**Pst Cln Slv 1**	2
Fill Speed	2.5uL/s	2.5uL/s		**Pst Cln Slv 2**	2
Fill Stroke	0	0			
Pull Up Delay	500ms	500ms			
Inject Speed	10uL/s	10uL/s			
Pre Inj Del	0ms	0ms			
Pst Inj Del	0ms	0ms			

Attachment IV: Chromatograms (ZB-1MS Column/Hydrogen Carrier Gas)

FIGURE 1: A1016 at 0.500ug/mL Plot

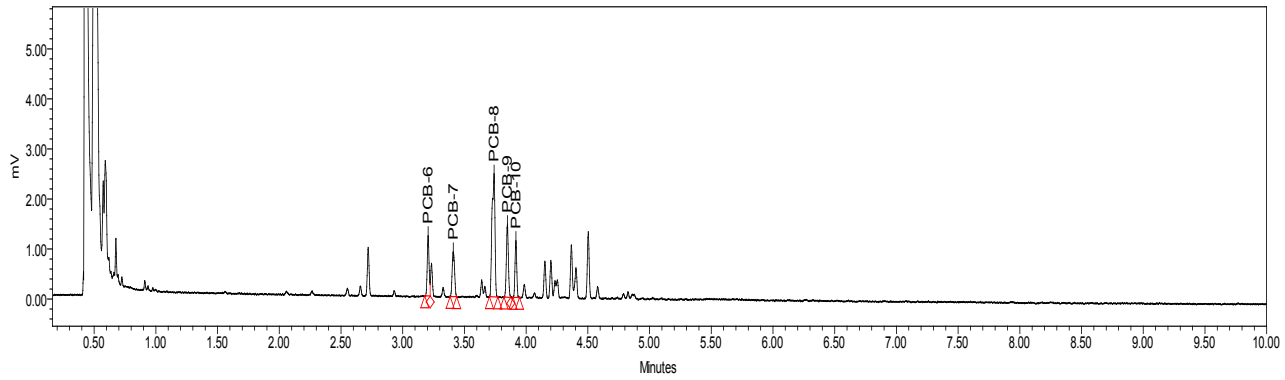


FIGURE 2: A1221 at 0.500ug/mL Plot

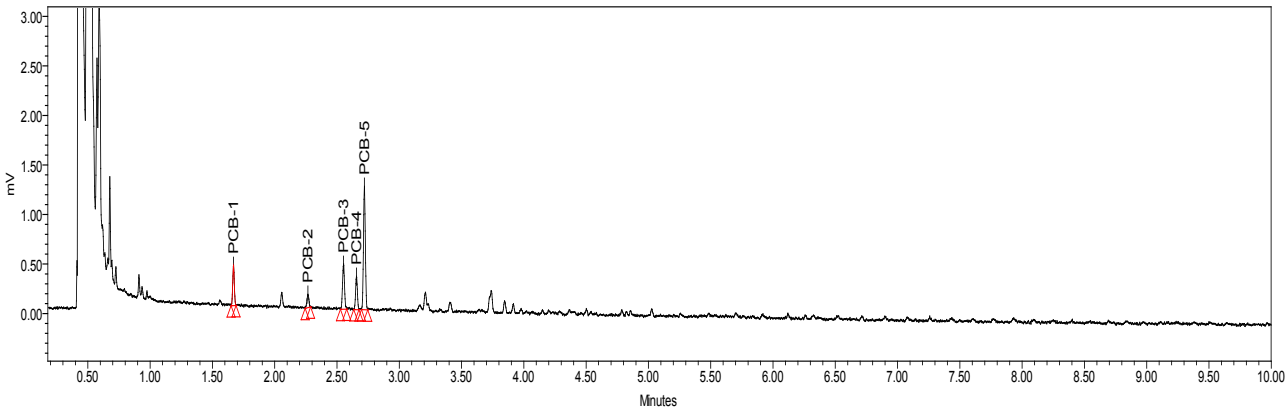
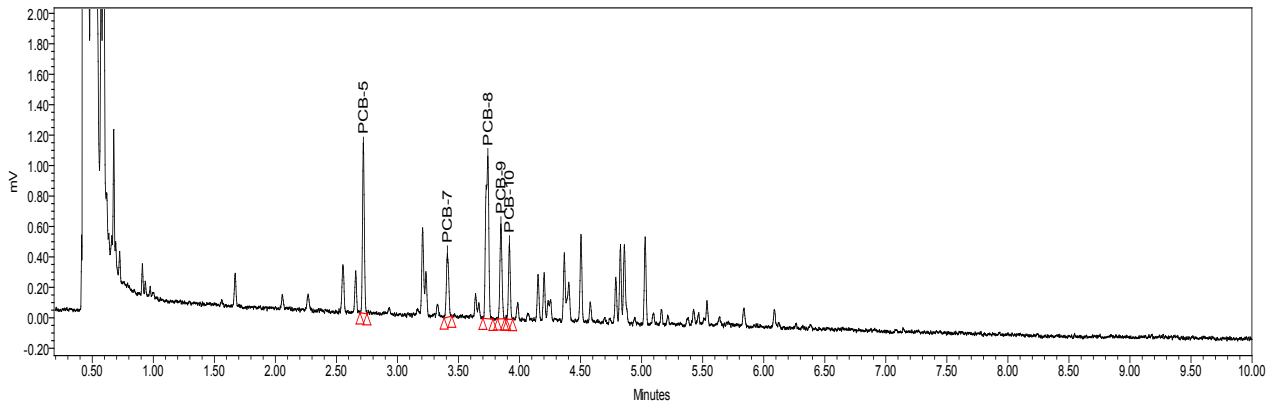


FIGURE 3: A1232 at 0.500ug/mL Plot



Attachment IV: Chromatograms (ZB-1MS Column/Hydrogen Carrier Gas) (continued)

FIGURE 4: A1242 at 0.500ug/mL Plot

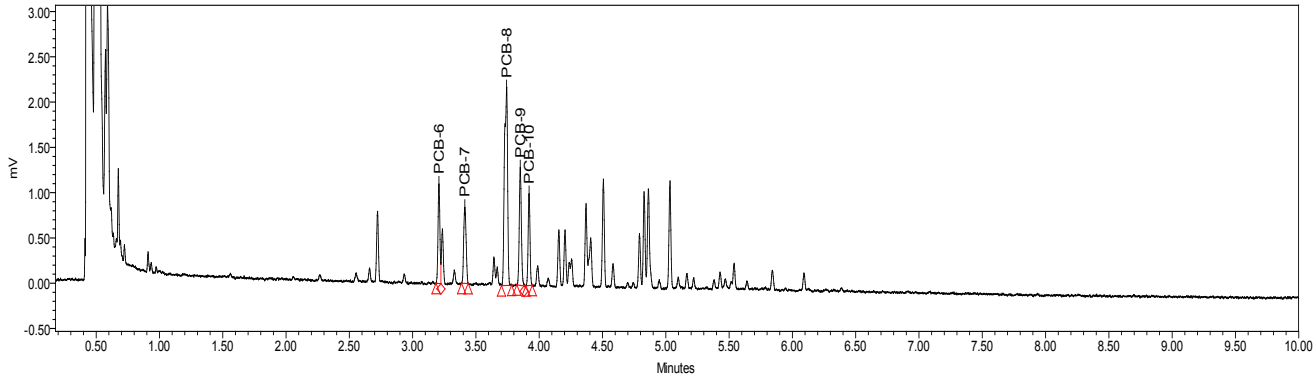


FIGURE 5: A1248 at 0.500ug/mL Plot

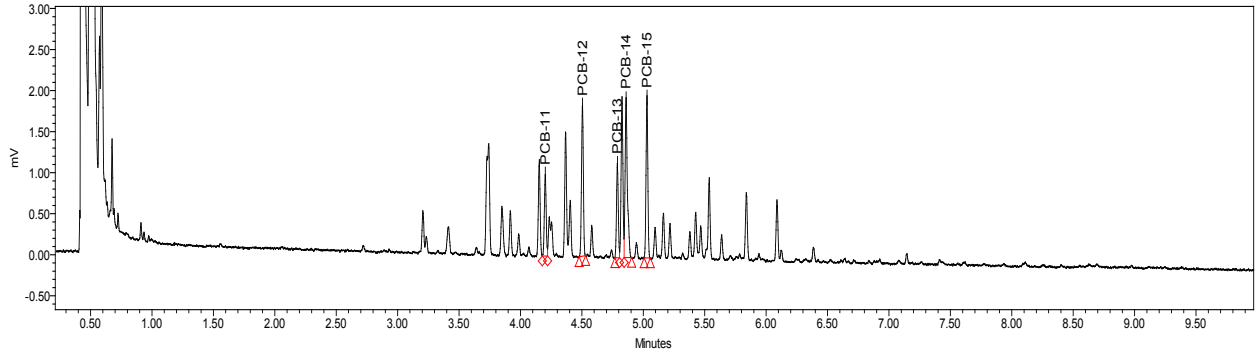
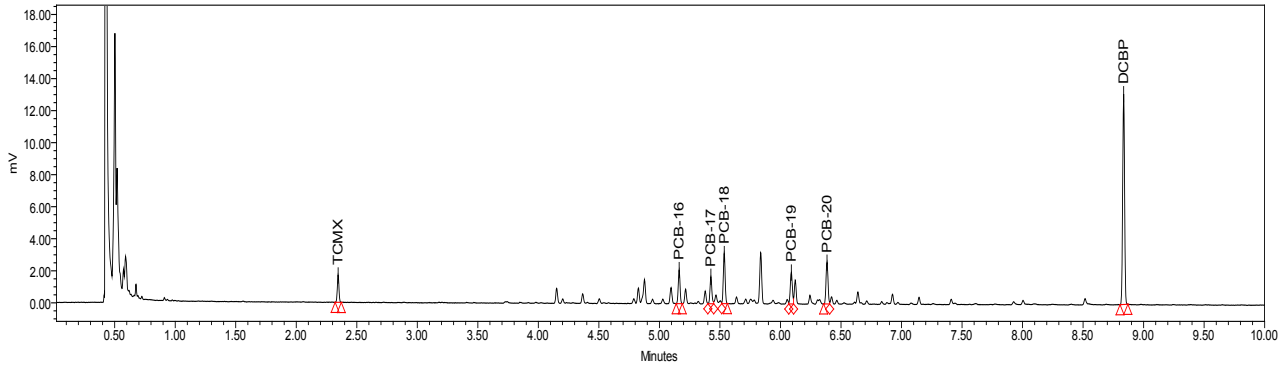


FIGURE 6: A1254 at 0.500ug/mL w/ TCMX & DCBP at 10/100ug/L Plot



Attachment IV: Chromatograms (ZB-1MS Column/Hydrogen Carrier Gas) (continued)

FIGURE 7: A1260 at 0.500ug/mL Plot

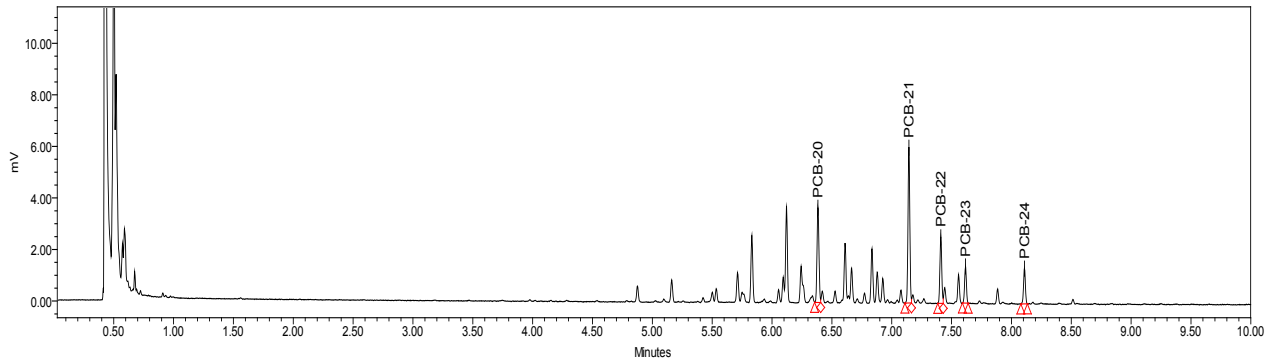


FIGURE 8: A1262 at 0.500ug/mL Plot

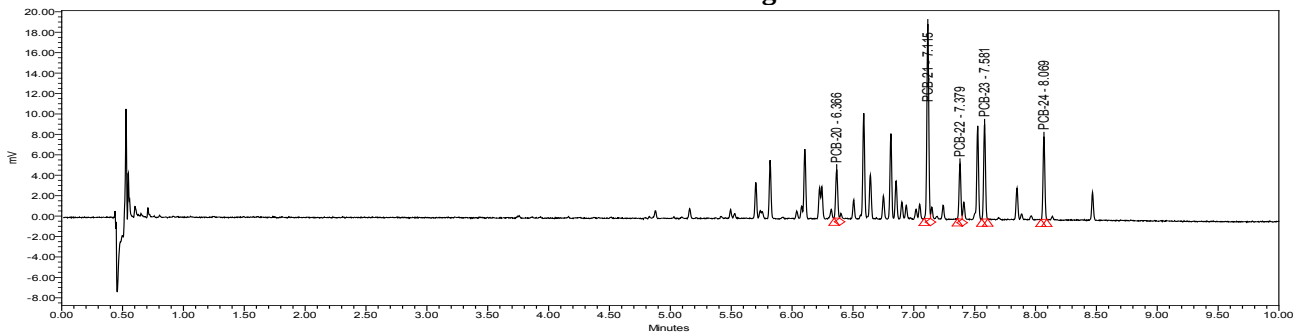
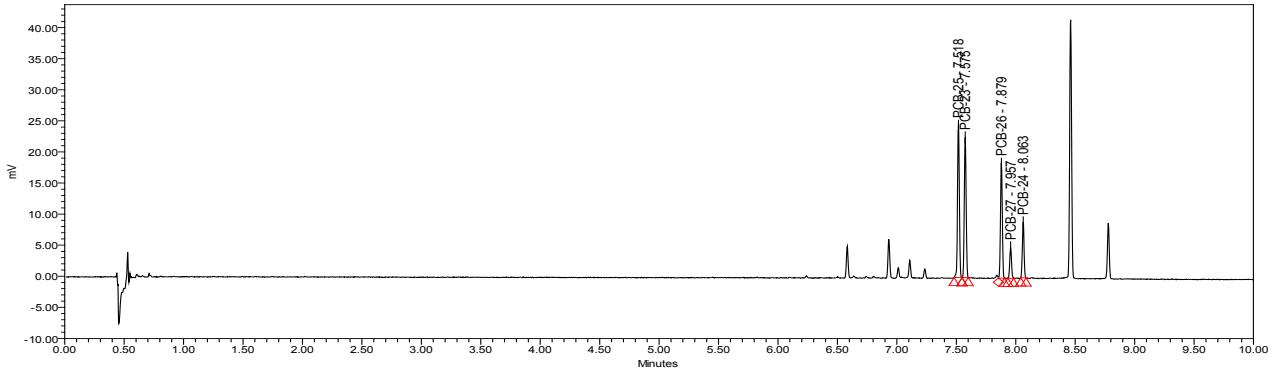


FIGURE 9: A1268 at 0.500ug/mL Plot



STANDARD OPERATING PROCEDURE

SULFUR CLEANUP

Reference Methods: EPA Method 3660B

SOP Number:	S-NY-O-337-rev.01
Effective Date:	07/08/15
Supersedes:	S-NY-O-337-rev.00

APPROVALS

Assistant General Manager	07/08/15 Date
Quality Manager	07/08/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

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Signature	Title	Date
Signature	Title	Date

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TABLE OF CONTENTS

SECTION PAGE

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to describe the process of performing sulfur cleanup of sample extracts using either copper or TBA (tetrabutylammonium) sulfite.

2. Summary of Method

2.1. The sample extract to undergo sulfur cleanup is mixed with either copper or TBA sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the sulfur cleanup of sample extracts using copper or TBA sulfite.

3.2. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. The copper technique for sulfur cleanup requires that the copper be very reactive, as evidenced by a shiny appearance. Care must be taken to remove any acid used to prepare the copper, in order to avoid degradation of some analytes.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Not applicable to this SOP.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. **Vials:** glass, 40mL and 4 dram (with Polyseal cap) for sample extracts.

9.2. **Vial Rack:** Plastic rack used to hold vials, during all phases of the extract processing.

9.3. **Wrist Shaker:** Burrell wrist action shaker, Model 75 and 88 (or equivalent).

9.4. **Pipettes:** S/P Disposable Serological Borosilicate Pipettes: 1mL, 5mL, 10mL.

9.5. **Fisher Pasteur Borosilicate glass pipette:** 9" #72050 (or equivalent).

10. Reagents and Standards

10.1. Pretreated Copper Granuales: Used for removal of sulfur. Restek Brand 26136 (or equivalent)

10.2. 2-Propanol: Used in TBA removal of sulfur. JT Baker 9095-03 (or equivalent)

10.3. Sodium Sulfite: Used to make TBA as well as the removal process. Sigma 239321-2.5kg (or equivalent)

10.4. TBA reagent: Used to make TBA solution. Sigma 155837-1kg (or equivalent)

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

12.1. **Cleanup using Copper:**

12.1.1. Transfer entire extract (generally 10 or 25 mL depending on the required analysis) into a calibrated centrifuge tube.

12.1.2. Add approximately 2g of clean copper to the sample extract. Vigorously mix the extract and the copper for at least 30 minutes. Allow the phases to separate.

12.1.3. Separate the extract from the copper by drawing off the extract with a disposable pipette and transfer to a clean vial. Repeat step 12.1.2 as necessary or transfer extract to GC analyst for analysis.

12.2. **Cleanup using TBA:**

12.2.1. Add 1mL of TBA sulfite reagent, 2mL of 2-propanol, and approximately 0.65g of sodium sulfite crystals to the extract and shake until a solid residue remains after repeated shaking. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots (approximately 0.65 g) to the extract and observe.

12.2.2. Place the samples on the wrist shaker for approximately 30 minutes observing at 15 minute intervals to make sure that the sodium sulfite is not consumed. Add 5mL of organic free water and shake for an additional 15 minutes.

12.2.3. Transfer the hexane layer to a new 40mL vial and cap.

13. Quality Control

13.1. If this cleanup procedure is performed on client samples, then all associated batch quality control samples (MB, LCS, MS/MSD) must also be taken through this clean up procedure.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Section 12.1: the entire extract is cleaned up instead of transferring 1mL of extract to a separate container for cleanup.

19.2. Section 12.2: the entire extract is cleaned up instead of transferring 1mL of extract to a separate container for cleanup. Because of this, the lab also shakes the sample extract for an additional 30 minutes instead of 1 minute as stated in the method.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Not applicable to this SOP.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. SW-846 Method 3660B, Sulfur Cleanup.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-NY-O-337-rev.00	First issue.	29Jan2015
S-NY-O-337-rev.01	General: corrected spelling and grammar errors Section 10.1: updated Vendor information Section 12.1.1: changed to document clean-up of entire extract	08July2015

Pace Analytical	Document Name: SOP Interim Change Form	Document Revised: 01-05-2016 Page 1 of 1
	Document No.: F-NY-Q-111-Rev.00	Issuing Authority: Pace Schenectady Quality Office

SOP Interim Change Form

Effective Date: 1/6/2016 **Initiated By:** PS

SOP Name and Number: S-NY-O-338-rev.00 Sulfuric Acid Cleanup

Reason for Change: adding allowance for use of concentrated sulfuric acid for complex matrices

SOP Section(s): 12.1.1 (Section Added)

New Procedure: The 1:1 sulfuric acid may be insufficient to fully clean-up samples of a more complex or non-routine matrix, including, but not limited to, tissue or building materials. In these instances, concentracted sulfuric acid may be used in place of 1:1 sulfuric acid at the discretion of the department supervisor. Additionally, some client programs or project specifications may require the use of concentracted acid.

The above stated procedure supercedes and replaces the referenced SOP Name, Number, and Section. Changes documented within this Interim Change Form are required to be incorporated into the next revision of the applicable SOP.

Quality Manager Approval: _____ **Date:** 1/6/2016

Laboratory Directory Approval: _____ **Date:** 1/6/2016

By Signing below, you acknowledge that you:

1) **Have read and understand the new procedure as stated above**
2) **Agree to abide by the procedure as stated above**
3) **Have access to the above stated SOP and this Interim Change Form**
4) **Understand that it is your responsibility to discuss any questions or concerns you have regarding the above stated SOP changes with your Supervisor or QA.**

Printed Name:	Signature:	Date:
Linge Brown	Linge Brown	1/6/16
Nicholas Conway	Nicholas Conway	1/7/16
Kuda Chinhoyi	Kuda	1/7/16
Melissa Harris	Melissa Harris	1/7/16
Kelly Sableski	Kelly Sablesk	1/11/16

STANDARD OPERATING PROCEDURE

SULFURIC ACID CLEANUP

Reference Methods: EPA Method 3665A

SOP Number:	S-NY-O-338-rev.00
Effective Date:	02/20/15
Supersedes:	First issue

APPROVALS

Assistant General Manager	Date: 02/20/15
Quality Manager	Date: 02/18/15

PERIODIC REVIEW

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Signature	Title	Date
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SECTION PAGE

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to describe the process of performing sulfuric acid cleanup of sample extracts for PCB analysis.

2. Summary of Method

2.1. An extract is solvent exchanged to hexane and the hexane extract is treated with sulfuric acid to remove interferences.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the sulfuric acid cleanup of sample extracts.

3.2. **Parameters**: This cleanup can only be used on PCB extracts. This cleanup method will destroy most organic chemicals such as Pesticides.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Not applicable to this SOP.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Not applicable to this SOP.

10. Reagents and Standards

10.1. Not applicable to this SOP.

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

12.1. Add approximately 5.0mL of 1:1 sulfuric acid to the sample extract and shake for 30 seconds by hand then centrifuge for approximately 2 minutes. Transfer the hexane (upper) layer to a clean 40mL vial. Be careful not to include any of the acid layer.

12.2. Repeat 12.1 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note:** All colored material may not be removed from the extract.

12.3. The extract is now ready for additional cleanup procedures or for GC analysis, as applicable.

13. Quality Control

13.1. If this cleanup procedure is performed on client samples, then all associated batch quality control samples (MB, LCS, MS/MSD) must also be taken through this clean up procedure.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Section 12.1: the entire extract is cleaned up instead of transferring 1mL of extract to a separate container for cleanup.

19.2. The lab does not perform the second hexane extraction as described in EPA Method 3665a sections 7.1.9 – 7.1.10. Acid Cleanups are performed on Hexane extracts which have been previously adjusted volumetrically to a fixed volume, typically 5 mL, 10 mL or 25 mL .

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Not applicable to this SOP.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, “Quality Systems”- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, “Quality Systems”- most current version.

25.4. SW-846 Method 3665A, Sulfuric Acid Cleanup.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-NY-O-338-rev.00	First issue.	29Jan2015

STANDARD OPERATING PROCEDURE

FLORISIL CLEANUP

Reference Methods: EPA Method 3620C

SOP Number:	S-NY-O-340-rev.00
Effective Date:	02/28/15
Supersedes:	First issue

APPROVALS

Assistant General Manager — Date: 02/28/15

Quality Manager — Date: 02/25/15

PERIODIC REVIEW

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Signature	Title	Date

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SECTION PAGE

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to describe the process of performing Florisil cleanup of sample extracts.

2. Summary of Method

2.1. A quantity of Florisil solid is added to sample extracts to remove unwanted materials (polar materials, water, and excess acid).

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the florisil cleanup of sample extracts.

3.2. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Not applicable to this SOP.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Clean vials for final extracts after Florisil cleanup.

9.2. Spatula.

9.3. Disposable Pasteur pipettes.

10. Reagents and Standards

10.1. Florisil - J.T. Baker #M368-08, 10% deactivated, solvent washed and deactivated as per SOP S-NY-O-283.

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

12.1. The Florisil slurry removes co-extracted polar compounds, residual water, and residual acid. This step is normally done after the Sulfuric Acid cleanup, but can be done again after the TBA shake to remove any residual water.

12.2. Add approximately 3g of tested and approved 10% deactivated Florisil to each vial containing the sample extract.

12.3. Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker. Swirl to get any Florisil off the walls of the vial, and then allow to settle.

12.4. Transfer the hexane layer to a clean 40mL vial.

13. Quality Control

13.1. If this cleanup procedure is performed on client samples, then all associated batch quality control samples (MB, LCS, MS/MSD) must also be taken through this clean up procedure.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Florisil is added directly to the sample extracts. Neither of the two options listed in the method (column or cartridge) are directly used.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. The extraction technician should have received in-house safety training and should know the location of first aid equipment and the emergency spill/cleanup equipment before handling any apparatus or equipment.

22.2. Safety glasses, a lab coat, and gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been classified as a known or suspected carcinogen. The extraction technician must review the Safety Data Sheets (SDS) for PCBs and all reagents used in the procedure before beginning the extractions.

22.3. All equipment and solvents should be handled within a laboratory fume hood.

23. Waste Management

23.1. Please see SOP S-NY-W-054 for details.

24. Pollution Prevention

24.1. Please see SOP S-NY-S-168 for pollution prevention measures.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, “Quality Systems”- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, “Quality Systems”- most current version.

25.4. SW-846 Method 3620C, Florisil Cleanup.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Not applicable to this SOP.

27. **Revisions**

Document Number	Reason for Change	Date
S-NY-O-340-rev.00	First issue.	21Feb2015

WORK INSTRUCTION FOR

Microwave Extraction of Base Neutral & Acids (BNAs) in Solid

Method: EPA 3546

Project Specific Requirement for Sparrows Point

SOP NUMBER:	WI-PGH-O-039-0
REVIEW:	D. Cavalier
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	Initial Release
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	02/17/16 Date
Senior Quality Manager	02/16/16 Date
Department Manager/Supervisor	02/16/16 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____and is ___**CONTROLLED or** __**UNCONTROLLED.**

TABLE OF CONTENTS

1. Purpose/Identification of Method

   1.1 This procedure documents the steps to be used to prepare solid samples for organic compounds by microwave extraction, according to EPA Method 3546.

2. Summary of Method

   2.1 An aliquot of sample is extracted with an organic solvent using the microwave extraction unit.

3. Scope and Application

   3.1 This procedure is applicable to extraction and concentration of semivolatile organics from solids. Samples may be prepared by this method for analysis by SW-846 Methods 8270C/8270D (PGH-O-001).

   3.2 Additional cleanup procedures that may be required for some sample extracts are described in the analytical SOPs.

   3.3 This procedure is restricted to use by, or under the supervision of, analysts experienced in preparation of extracts for chromatographic analysis. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

   4.1 Solid samples.

5. Limit of Detection and Quantitation

   5.1 Not Applicable.

6. Interferences

   6.1 Solvents, reagents, glassware and other sample processing equipment may yield artifacts and/or interference's to sample analysis. All glassware must be rinsed immediately after use with an appropriate solvent (i.e. the solvent used to extract or bring the sample to final volume). Any glassware or equipment which comes into contact with samples or extracts must be carefully cleaned with a lab glass washing detergent solution. Copious amounts of hot tap water must be used to rinse the glassware to ensure that all soap residues have been removed. Glassware is then thoroughly rinsed with deionized water followed by an acetone rinse to remove any residual water/organic residue from the glassware.

   6.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to matrix interference, further cleanup of the sample extract may be necessary.

   6.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Phthalates are commonly used as plasticizers in plastics and are easily extractable from such materials. All personnel wearing gloves must exercise great care in the handling of extraction glassware, reagents, and sample containers and samples in order to minimize phthalate contamination. All laboratory equipment must be checked for the use of flexible tubing which may contain phthalates.

   6.4 Soap residue (e.g., sodium dodecyl sulfate), results in a basic pH on glassware surfaces and may cause the degradation of certain analytes. Specifically, Aldrin and Heptachlor will degrade in this situation.

7. Sample Collection, Preservation, and Handling

   7.1 Plastic containers may not be used for the storage of samples for organic analysis due to possible contamination from phthalate esters and hydrocarbons within the plastic

7.2 A minimum of 15g of solid material should be provided for each test by the client for analysis. Sample aliquots smaller than 15g may result in elevated detection limits. Additional volume should be provided for Matrix Spike (MS) and Matrix Spike Duplicate (MSD) samples.

7.3 Samples are to be stored ≤6 °C.

7.4 Sample Extraction/Analysis:

7.4.1 Samples must be extracted within 14 days from the date of collection and analyzed within 40 days from the date of sample extraction.

7.5 Extracts are to be stored at ≤6 °C in the designated refrigerator.

7.5.1 Sample extracts for EPA Method 8270C are to be stored at -10°C.

7.5.2 Sample extracts for EPA Method 8270D are to be stored at ≤6 °C.

7.5.3 Sample extracts must not be stored with any stock standards, working standards, neat materials, solvents or waste.

7.6 Extraction personnel shall notify the Department Manager/Supervisor and/or the Project Manager/Coordinator regarding any samples that do not conform to the collection requirements. The Department Manager/Supervisor and/or the Project Manager/Coordinator will advise the analyst on how to proceed with the extraction. This may include extracting lower amounts of sample and raising detection limits, lowering the final volume, or waiting for more sample volume to be collected.

7.7 Any non-conformances will be documented in the extraction logs and in the final report.

8. Definitions

8.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, Inc. Quality Manual for the definitions used throughout this SOP.

9. Equipment and Supplies

9.1 Microwave Extraction System, CEM MarsXpress, Model MARS 230/60, model #907501 (75mL volume, 40 position), or equivalent.

9.2 Microwave Vessels, 75mL, or equivalent.

9.3 Microwave Vessel Rack, 40 position unit, or equivalent.

9.4 Filter Paper, Whatman No. 41, or equivalent.

9.5 Spatulas, wooden.

9.6 Analytical Balance, capable of weighing ±0.01g.

9.7 Bottle Top dispenser, capable of dispensing 25mL of solvent.

9.8 Syringes, various sizes, Hamilton, or equivalent

9.9 Glass funnels.

9.10 Disposable Pasteur pipettes.

9.11 Zymark Turbo-Vap® concentration system, or equivalent.

9.12 Zymark Turbo Vap® concentration tubes, or equivalent.

9.13 Volumetric flasks, 1, 5 and 10mL, Class A, glass.

9.14 Vials: 5mL amber glass with PTFE-lined screw caps.

9.15 Oven capable of reaching 400°C minimum.

9.16 Graduated cylinder, 10mL, Glass, TC.

10. Reagents and Standards

10.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.2 Sodium Sulfate (granular, anhydrous), Na_2SO_4, methylene chloride rinsed.

10.3 Hydromatrix (diatomaceous earth), methylene chloride rinsed.

10.4 Ottawa Sand: Purify by heating at least 400°C for at least 4 hours in a shallow tray or crucibles.

10.5 Methylene chloride, CH_2Cl_2: Fisher Optima® grade quality, or equivalent.

10.6 Acetone, CH_3COCH_3: Fisher Optima® quality, or equivalent.

10.7 Methanol, CH_3OH: Fisher Optima® grade quality, or equivalent.

10.8 Surrogate standard and matrix spiking solutions: Standards for use as surrogate and spiking solutions are prepared from purchased certified solutions at the concentrations listed in Attachment No. 1.

10.8.1 All stock standards are stored until the expiration date at the appropriate temperature according to the manufacturer's recommendation.

10.8.2 Working standards are stored at ≤6 °C, in amber glass vials or bottles, for six months from the date of preparation or the manufacturer's expiration date for the stock standard, whichever occurs first.

10.8.3 Purchased, commercially prepared stock solutions are certified by the manufacturer or independent source. Certificates of Analysis are maintained within the laboratory.

10.8.4 An aliquot of each surrogate and matrix spike solution is sent to the appropriate analytical department for verification when the solution is prepared. New surrogate and matrix spike solutions are not to be used in the extraction lab until the verification has been completed.

10.8.5 See the organic preparation standard logbook for guidance on the specific steps for the use of the purchased stock solutions and dilutions required to make surrogate and spike solutions listed in Attachment No.1.

10.9 NOTE: the concentrations listed in Attachment No. 1 are the concentrations of the actual solutions used to do the spiking. The final "true values" are dependent on the initial sample weight and the final volume of the extract.

11. Calibration and Standardization

11.1 Refer to the MARS Microwave Operations Manual for Power Test information, including recommended testing frequency and troubleshooting information.

12. Procedure

12.1 Glassware is cleaned in accordance to Standard Operating Procedure PGH-C-009 prior to the start of any extraction.

12.2 Retrieve the samples to be extracted from cold storage. Determine if enough

sample volume has been provided to complete a Matrix Spike and Matrix Spike Duplicate.

12.3 Complete the required information fields in the logbook for the batch to be extracted, including the extraction start time.

12.3.1 Record any applicable comments, such as limited sample volume, unusual sample consistency, color or odor of the sample, in the area provided for each sample.

12.3.2 If enough sample volume was not provided to extract an MS and MSD, record the following statement in the logbook, “insufficient sample provided for MS/MSD”.

12.3.3 Continue to record any appropriate comments regarding the sample batch throughout the extraction process for inclusion in the project internal file or case narrative, such as the inability to concentrate the extract to the final volume required by the analytical method.

12.4 Inspect each of the 75mL microwave extraction vessels to ensure that they are clean and dry. Pre-rinse the extraction vessels with acetone then methylene chloride. Discard the rinses as waste. Label the extraction vessels with the workorder, sample number and the test method performed.

12.5 Weigh a 15g aliquot of each sample into a clean weigh dish, removing twigs, rocks and other foreign material (refer to SOP ALL-Q-021, Subsampling (Sample Homogenization)). Record the mass to the nearest 0.01g.

12.5.1 A reduced amount of sample may be used if sample matrix is suspected to be an issue. Examples of sample matrices that could be suspected to cause issues are, but not limited to, cloth, mulch, and samples containing high metal content.

12.6 Add a sufficient amount of rinsed Hydromatrix® to each sample aliquot and mix to ensure that the sample is dry.

12.7 Transfer the sample aliquot to an extraction vessel and push the sample to the bottom to any remove air pockets.

12.8 For each batch of samples (up to 20 samples), prepare a method blank (MB) and a Laboratory Control Sample (LCS) using Ottawa sand as the matrix. Add an aliquot of rinsed Hydromatrix® to the method blank and the LCS.

12.9 Add the required amount of surrogate solution to all samples and the appropriate spiking solution to the LCS and MS/MSD samples (Table 1).

12.9.1 If required by the client, a full list of target analytes will be spiked which may necessitate multiple LCS samples being extracted.

12.10 Immediately add 25mL of methylene chloride to each extraction vessel, then add the vessel plug and screw on the vent cap. Tighten the cap using the capping station. The capping station has a preset torque and does not require adjusting.

12.11 Insert each vessel into a high pressure microwave sleeve. Make sure that the sleeve is pushed up tight against the bottom of the vessel cap.

12.11.1 Failure to ensure that the protective sleeve is properly positioned can result in a high pressure vessel explosion during the extraction process.

12.12 Add the vessels to the microwave carousel. Make sure the vessels are evenly spaced around the carousel in order for the heating sensors to work properly. This only becomes necessary if you have less than a full circle of vessels in the carousel.

12.13 Turn on the microwave extractor and (based on the number of vessels in the microwave carousel) choose the appropriate method for extraction.

12.13.1 If the number of vessels is between 1-24, choose the method titled "Organics 1.24". This method is set as follows:

Power Setting: 1600W at 75%.

Ramp Rate: 10 minutes to a final temperature of 115°C.

Hold at 115°C for 10 minutes.

12.13.2 If the number of vessels is between 25-40, choose the method titled "Organics 25.40". This method is set as follows:

Power Setting: 1600W at 100%.

Ramp Rate: 10 minutes to a final temperature of 115°C.

Hold at 115°C for 10 minutes.

12.14 Press START on the microwave extractor.

12.15 After the microwave extraction is completed, allow the vessels to cool to room temperature (about 30 minutes). Vessels can remain in the extractor or they can be removed from the extractor to cool on the counter.

12.15.1 CAUTION: The extraction vessels are at an elevated temperature and pressure after the extraction stage. Allow the vessels to cool before opening.

12.16 Set up the required number of pre-cleaned TurboVap® tubes in the hood to collect the sample extracts. Use a permanent marker to label each tube with the workorder, sample number and the test method performed.

12.16.1 If the samples will not be immediately concentrated, set up pre-cleaned jars instead of TurboVap® tubes to collect the extracts in the hood.

12.17 Place the glass funnels in the tops of the TurboVap® tubes (or jars). Then place filter paper and add approximately 30g of sodium sulfate into the funnels. Rinse the sodium sulfate with 10-30mL of methylene chloride and discard the rinse.

12.18 Pour the sample extracts from the microwave extraction vessel through the filter paper into the appropriately labeled Turbo Vap® tubes (or jars).

12.18.1 Empty the solid contents of the microwave extraction vessel into the filter funnel. Rinse the extraction vessel three times with methylene chloride and add the rinses to the sample in the filter funnel.

12.19 The extracts may be concentrated immediately or the jar containing the extracts may be capped with a PTFE lined lid or tightly covered with foil. If the extracts will be concentrated at a later time, they should be stored at room temperature in the organic preparation laboratory.

12.20 Verify that the following conditions are set on the TurboVap® II Concentration Workstations:

Water Temperature: 30-35°C.
Nitrogen Pressure: 11psi or less.
End Point Select: Manual.

12.21 Also, verify that the water level in the TurboVap® is at a sufficient level to avoid condensation from forming in the extracts.

12.22 Place each turbo tube into one of the positions in the TurboVap® II

Concentration Workstations. Start the concentration process with the nitrogen pressure low enough to avoid splashing, which can result in cross contamination between samples. The nitrogen pressure may be increased as the extract concentrates, but must never exceed 11psi.

12.22.1 If concentrating samples that were previously extracted and placed in jars, rinse the required number of tubes with methylene chloride and label each one with the workorder, sample number and test method. Carefully pour the extract from the jar and into the appropriately labeled tube. Rinse the jar with 10-15mL of methylene chloride and add this rinse to the tube.

12.23 Concentrate each sample according to the requirements of the method, ensuring that the sample is not allowed to evaporate to dryness, by frequently checking the volume of the extract.

12.23.1 For all BNA 8270C/8270D methods, concentrate the extract to a volume approximately ¾ of the required final volume. Methylene chloride will be the finalizing solvent for these methods.

12.24 Label the appropriate vials with the workorder, sample number and test method. Extracts that have final volumes of 5mL or greater should be bottled in 4mL amber vials.

12.25 Depending on the final volume of the extracts, choose the appropriate size Class A volumetric flask or graduated cylinder and rinse them with methylene chloride , discarding the rinse.

12.26 Use a disposable pipette to quantitatively transfer the extract from the tube to a rinsed volumetric flask or graduated cylinder. Complete the transfer by rinsing the tube three times with a small amount of methylene chloride. Adjust the extract to the appropriate final volume with methylene chloride.

12.26.1 If water appears in the extract after concentration, dry the extract with a small amount of (methylene chloride rinsed) sodium sulfate before transferring the extract to the volumetric or graduated cylinder.

12.27 With a pipette, mix the extract within the volumetric or graduated cylinder to ensure that extract is homogenous.

12.28 Pipette the extract from the volumetric or graduated cylinder into the appropriately labeled vial. Cap the vial with a PTFE lined lid.

12.29 Record a finish time in the logbook and enter the extraction information into the LIMS.

12.30 Make a copy of the extraction information and deliver it along with the sample extracts to the appropriate analytical department for storage.

13. Quality Control

13.1 At least one method blank must be extracted with each batch of samples.

13.2 At least one LCS must be extracted with each batch.

13.3 At least one set of MS/MSD samples must be extracted per batch.

14. Data Analysis and Calculations

14.1 Concentrations of surrogate and matrix spiking solutions are prepared according to the following formula:

$$\text{Concentration } (\mu g/mL) = C_{A^*} V_A / V_S$$

Where:

C_A = Concentration of the stock solution, µg/mL.
V_A = Volume of the stock solution, mL.
V_S = Volume solution is diluted to, mL.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1 Not Applicable.

16. Corrective Actions for Out-of-Control Data

16.1 Not Applicable.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1 Not Applicable.

18. Method Performance

18.1 The ongoing analysis of spiked samples for each analytical method is used to evaluate and document data quality.

18.2 Prior to performing an extraction procedure for any analytical method without supervision, the preparation analyst must read and understand this SOP and complete an acceptable initial demonstration of capability (IDOC) study.

18.2.1 A Continuing Demonstration of Capability (CDOC) will be performed each year after the IDOC to demonstrate continued proficiency.

18.3 Performance Test (PT) samples are extracted and analyzed on an annual basis.

18.4 The instrument analyst or department manager/supervisor may request re-extraction of samples which do not meet acceptance criteria (i.e., low or high surrogate/spike recovery or blank contamination). If there is insufficient sample remaining for re-extraction, it will be documented in the project case narrative.

19. Method Modifications

19.1 Using 100% methylene chloride for the extraction instead of the method suggested 1:1 hexane/acetone solution.

19.2 Samples are not being ground to a fine powder due to possible loss of target analytes.

20. Instrument/Equipment Maintenance

20.1 Zymark TurboVap® or equivalent concentration system

20.1.1 Temperatures are recorded daily for each system before use.

20.1.2 The reagent water in each system is changed monthly or sooner if necessary to avoid possible contamination.

20.1.2.1 Reagent water is added to each system daily to maintain a water level sufficient to avoid condensation from forming in the extract.

20.1.3 The “TurboVap® II Concentration Workstation Operators Manual” or appropriate instrument manual is referred to for details on the operation of the TurboVap® II Concentration Workstations and for troubleshooting problems.

20.2 Microwave Extraction System

20.2.1 Following the guidelines listed in the “MARS Operation Manual”, complete the microwave power measurement at least quarterly. If the microwave is not producing sufficient wattage, refer to the Troubleshooting Guide in the “MARS Operation Manual”.

20.3 The “MARS Operation Manual” is referred to for details on the operation of the microwave extraction system and for troubleshooting problems.

21. Troubleshooting

21.1 Not Applicable.

22. Safety

22.1 Refer to the Pace Analytical Services, Inc. (PASI) – Pittsburgh Chemical Hygiene Plan/Safety Manual (CHP/SM) for the specific safety requirements to be followed when working in the laboratory.

22.2 The extraction vessels are at elevated temperatures and pressure after the extraction stage. Allow the vessels to cool before opening.

22.3 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

22.4 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

23. Waste Management

23.1 All waste glassware (sample jars, extraction jars, solvent bottles, etc.) is collected in the receptacles provided in the Organic Preparation laboratory area. This waste is then disposed of according to applicable regulations.

23.2 Waste solvent and standard materials are collected in appropriate containers and regularly removed to waste drums located in a designated waste chemical storage area.

24. Pollution Prevention

24.1 Glass solvent containers must not exceed volumes of 4 liters.

24.2 An unbreakable carrier must be used to transport 4 liter glass containers of solvent from storage areas to the Organic Preparation Laboratory.

24.3 Solvents are transferred to smaller, labeled PTFE bottles for lab use.

24.4 Spills are promptly cleaned up using paper towels, sorbent materials or spill kits, depending on the amount of and specific substance spilled. Specific protocols for handling spills are found in the PASI Chemical Hygiene Plan and in the SDS.

25. References

25.1 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision)

25.2 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

25.3 Microwave Extraction, EPA Method 3546, Revision 0, February 2007.

25.4 “MARS Operational Manual”, CEM Corporation, Revision 2, February 2006.

25.5 Pace Analytical Services, Inc. - Pittsburgh Quality Assurance Manual, current version.

25.6 SOP PGH-C-032, Support Equipment, current version.

25.7 SOP PGH-C-037, Standard and Reagent Traceability, current version.

25.8 SOP PGH-Q-038, Laboratory Equipment, current version.

25.9 SOP PGH-Q-039, Corrective Action, current version.

25.10 SOP S-ALL-Q-028, Lab Track, current version.

25.11 SOP PGH-C-027, DI Water, current version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1 Attachment No. 1: Surrogate and Spike Solutions

26.2 Table 1: Extraction Volumes and Solvents (Per Method).

27. Revisions

Document Number	Reason for Change	Date
WI-PGH-O-039-0	Initial Release	17Feb2016

Attachment No. 1 - Surrogate and Spike Solutions

Semivolatile (8270C and 8270D) Surrogate Solution

Solvent: methanol

Acid Surrogate Standard Mix Analytes	Concentration (mg/L)
2-fluorophenol	75
phenol-d6	75
2-chlorophenol-d4	75
2,4,6-tribromophenol	75
B/N Surrogate Standard Mix Analytes	
1,2-dichlorobenzene-d4	50
nitrobenzene-d5	50
2-fluorobiphenyl	50
p-terphenyl-d14	50

- Working BNA Surrogate Standard Preparation

Add 250mL methanol, 5mL B/N Surrogate Standard Mix (3/90) and 5mL the Acid Surrogate Standard Mix (3/90) to a 500mL volumetric flask. Dilute to volume with methanol and mix by capping the volumetric and inverting it several times. The final concentration of the solution is 50/75mg/L (BN/Acids). Refer to Table 1 for the appropriate sample spiking amounts.

Semivolatile (8270C and 8270D) Matrix Spike Solution

Solvent: methanol

8270 BNA Custom Mix w/o Pesticides	**Concentration (mg/L)**
2-chlorophenol	100
2,4-dimethylphenol	100
4-nitrophenol	100
2,4-dichlorophenol	100
4-chloro-3-methylphenol	100
2-methyl-4,6-dinitrophenol	100
2-nitrophenol	100
2,4-dinitrophenol	100
2,4,6-trichorophenol	100
phenol	100
2-methylphenol	100
4-methylphenol	100
2,4,5-trichlorophenol	100
N-nitrosodimethylamine	100
2,4-dinitrotoluene	100
2,6-dinitrotoluene	100
isophorone	100

benzoic acid	100
azobenzene	100
butyl benzyl phthalate	100
diethyl phthalate	100
dimethyl phthalate	100
di-n-butyl phthalate	100
di-n-octyl phthalate	100
4-bromophenyl phenyl ether	100
1,2-dichlorobenzene	100
1,3-dichlorobenzene	100
1,2,4-trichlorobenzene	100
benzyl alcohol	100
aniline	100
4-chloroaniline	100
2-nitroaniline	100
3-nitroaniline	100
4-nitroaniline	100
acenaphthene	100
acenaphthylene	100
benzo(b)fluoranthene	100
benzo(k)fluoranthene	100
benzo(ghi)perylene	100
chrysene	100
fluoranthene	100
fluorene	100
naphthalene	100
phenanthrene	100
2-methylnaphthalene	100
carbazole	100
3,3’-dichlorobenzidine	100
anthracene	100
benzo(a)anthracene	100
benzo(a)pyrene	100
bis(2-chloroethoxy)methane	100
bis(2-chloroethyl)ether	100
bis(2-chloro-1methylethyl)ether	100
bis(2-ethylhexyl)phthalate	100

4-chlorodiphenyl ether	100
2-chloronaphthalene	100
dibenz(a,h)anthracene	100
dibenzofuran	100
1,4-dichlorobenzene	100
hexachlorobenzene	100
hexachlorobutadiene	100
hexachlorocyclopentadiene	100
hexachloroethane	100
indeno(1,2,3-cd)pyrene	100
nitrobenzene	100
N-nitrosodi-n-propylamine	100
N-nitrosodiphenylamine	100
pentachlorophenol	100
pyrene	100

Custom 8270 BNA Mix	**Concentration (mg/L)**
pyridine	100
2-picoline	100
decane (C10)	100
acetophenone	100
N,N-diethylaniline	100
a-terpineol	100
1-methylnaphthalene	100
1,3-dinitrobenzene	100
2,3,4,6-tetrachlorophenol	100
benzidine	100
n-octadecane (C18)	100
caprolactam	100
atrazine	100
biphenyl	100
4-chlorobenzotrifluoride	100
2,3-dichloroaniline	100
1,2,4,5-tetrachlorobenzene	100

Benzaldehyde Solution	**Concentration (mg/L)**
benzaldehyde	100

- Working BNA Spiking Standard Preparation

Add 35mL methanol, 5mL 8270 BNA Custom Mix w/o Pesticides, 2.5mL Custom BNA Mix and 2.5mL Benzaldehyde Solution to a 50mL volumetric flask. Dilute to volume with methanol and mix by capping the volumetric and inverting it several times. The final concentration of the solution is 100mg/L. Refer to Table 1 for the appropriate sample spiking amounts.

TABLE 1 - Extraction Volumes and Solvents (Per Method)

Analytical Method	Initial mass (g)	Surrogate Spike (mL)	LCS/ Matrix Spike (mL)	Extraction solvent	Final Vol. (mL)	Exchange Solvent
BNA 8270C/8270D	15	0.5	0.5	CH_2Cl_2	5	NA

APPENDIX C

Data Management Plan

Data Management Plan

This section presents the approach and procedures that will be used to document and track the data and results of Phase II Investigations (or other similar environmental investigations) at the Sparrows Point facility. During the investigations, many different types of data will be collected (e.g., geologic data, groundwater data [both physical and chemical], soil data, etc). The systems and procedures described in this section will help enhance and ensure the accuracy of these data and provide a mechanism for their efficient collection, storage, retrieval, evaluation, and presentation. Following an overview of the data management approach, project documentation, electronic data specifications, and database structure are described.

1 OVERVIEW

A database system will be established and used to manage the process of data collection, handling, control, storage, access, reduction, and evaluation throughout the investigations. The database system will store most of data in Microsoft Access database files, but also in a system of folders on an ARM server. ARM will receive copies of all sampling data generated during Phase II investigations, although the sampling and reporting activities throughout the site will be carried by a number of different consultants.

The database system will be an information system capable of supporting:

- Data entry, including file conversion from commonly accepted formats (e.g., Access and Excel), electronic deliverables from analytical laboratories, and manual entry of field data (both directly to laptops and remotely from standardized collection/entry forms);
- Data management and storage (internal file conversion and data standardization);
- Data retrieval for standardized report formats; and
- Data output to commonly accepted formats for environmental characterization and monitoring activities being performed during Phase II investigations.

1.1. Phase II Investigation Data Management Objectives and Scope

The objectives of the data management process are as follows:

- Standardize and facilitate the collection and transfer of field-generated data to the database system.

- Provide a structured data set that will support environmental investigation planning and decision-making.
- Minimize the uncertainties associated with the data, data-derived products, and interpretation of results through quality assurance and quality control (QA/QC) defined measures and practices.
- Ensure the accessibility of environmental data for environmental characterization, report generation, risk assessments, and other environmental needs.
- Ensure that data are adequately documented with descriptive information to ensure the technical defensibility and legal admissibility of the data.

The scope of the data management activities addressed by this plan includes, but is not limited to:

- Modification, operation, and maintenance of the database system to organize and store current environmental information generated by Phase II investigations and historical information;
- Implementation and modification of a field data entry system for transferring of field data into the database system;
- Incorporation of historical data into the database system;
- Management of project documentation (hard or electronic copy);
- Standardized electronic data deliverables; and
- Protection of data through standardized methods to ensure data integrity.

1.2. Data Management Roles and Responsibilities

The functional responsibilities of the data management team are described below; the responsibilities are identified by titles but are not necessarily individual staff positions.

- **Data management specialists** have broadly defined multidisciplinary responsibilities. Their tasks may include the following:
    - Responsible for the proper execution of the data management process, and to identify relevant data, ensure that data are complete and consistent, and resolve problems associated with data.
    - Oversee contracted analytical and data validation services, which may include pre-award auditing and review, coordination of the project/laboratory/data validation interfaces, and continuing performance review of the laboratory and data validator.

  - Participate in QA/QC activities, including nonconformance investigations and reports and QA reviews. When coordinating data support for the multidisciplinary technical team, prepare work agreements as necessary, review sample receipt acknowledgments, and receive laboratory and data validator data packages.
  - Conduct verification activities following receipt of electronic data and participate in QA/QC activities to resolve nonconformance as necessary.
  - Evaluate the effectiveness of QA activities through surveillance; help resolve quality problems; and ensure that corrective actions are taken and appropriately documented.
  - Manage the recorded information about project activities that is keyed input into the data management system.

- **Database administrators** have overall responsibility for the design, operation, and maintenance of the databases. They also control the interface between data entry programs and databases. Some database administrators also will serve as programmers who are responsible for designing, developing, and implementing databases and data entry tools.
- **Field Scientists/Personnel** help prepare the work plan and implement it in the field; prepare for and coordinate sampling activities; oversee the collection, recording, and documentation of the field data; and ensure that chain-of-custody forms are completed correctly. The field personnel also compile and perform QC checks on field data.
- **Project engineers and scientists** perform statistical summaries of physical and chemical data by medium, location, and sampling event, and present these summaries in tables, charts, graphs, and maps. The data are examined for consistency with the data collection quality assurance procedures described in Section 4. The analysts identify anomalies in the data and determine whether corrections or qualifiers are required, performing statistical analyses as needed, and prepare data for input to numerical models.
- **GIS applications specialists** prepare maps that illustrate geographical features and area characteristics, such as topography, land use, ground cover, roads, buildings, and hydrography; digitize existing maps; edit and format spatial data, combine them with attribute data from the project database; and display results through graphic outputs that include maps, color displays, and tabular information.

2 PROJECT DOCUMENTATION

A large variety of technical data currently exist from previous environmental investigations and the operations of existing interim measures. These data exist in a variety of media, including printed and electronic reports with data, maps, figures, and tables. BSC and various consultants have generated this information over approximately 25 years. Significant amounts of additional data will be generated during the course of the Phase II investigations. A data document tracking system will be

maintained so that the general structure of the data is preserved. Project tracking data, schedules, progress reports, and field notes will be maintained to monitor, manage, and document the progress of the Phase II investigations.

2.1. General Data Records and Logs

Select data from past investigations and from the Phase II investigations will be compiled and summarized in tables. Types of data that will be tabulated include:

- Analytical data laboratory summaries;
- Data validation summaries;
- Well construction information;
- Well development information;
- Chain-of-custody records;
- Field-collected data; and
- Field logbooks.

2.2. Data Tracking

The status of all data generated during Phase II investigations will be recorded in a Sample Data Tracking file. This file will group data by general location within the Site and record dates of transfer between organizations. Every sample collected in the field will be listed in the Sample Data Tracking file. For each sample, the table will record the date of collection, the date that the sample is received by the laboratory, date Level 2 data package is sent to ARM from PACE, date Level 4 data package is sent to EDQI from PACE, and the date Data Validation Report is sent to ARM from EDQI.

2.3. Data Backup and Retention

All data stored on ARM servers will undergo a daily backup to an external drive. All data associated with the site-wide investigation will be retained for the entire duration of the project.

3 ELECTRONIC DATA SPECIFICATIONS

3.1. Laboratory Data

EAG has contracted PACE of Greensburg, Pennsylvania to perform the laboratory analysis for this project. The laboratory will provide full deliverable or CLP-equivalent data packages. Each data package from the laboratory will undergo an USEPA level 2B verification/validation review as outlined in "Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use", USEPA-540-R-08-005, January 2009. The verification/validation review will be conducted in accordance with **"**USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review**",** USEPA-540-R-08-01, 1 June 2008, and "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review", USEPA-540-R-10-011, January 2010.

The quality control requirements specified in the methods and associated acceptance criteria will also be used to evaluate the data.

Raw data will not be reviewed. The following items will be reviewed as part of the Level 2B validation:

- Data completeness;
- Technical holding times;
- Summaries of Instrument Performance Check Results;
- Summaries of Initial Calibrations;
- Summaries of Calibration Verification;
- Summaries of Blank Results;
- Summaries of Matrix spike and Matrix Spike Duplicate results;
- Summaries of Laboratory Duplicates (Inorganic Parameters Only);
- Summaries of Laboratory Control Samples;
- Summaries of Internal Standards;
- Field Duplicate Results;
- QC Blanks; and
- Overall assessment of data;

Upon completion of the data validation, Data Validation Reports (DVRs) will be prepared to present the data validation findings. A DVR will be prepared for each SDG data package reviewed. Analysis results forms, annotated by hand to reflect qualifier codes resulting from the data validation review, will be included with both the reports. These qualifier codes will be presented in the far right margins of the analysis results forms, and will be clearly identifiable. A glossary defining each data validation qualifier code will also be included with the report.

3.2. Sample Identification System

A sample identification (ID) system (or Station Designation Scheme) will be used to identify each environmental sample collected. This ID system will provide a tracking procedure so that information about a particular sample collected from a specific location can be retrieved easily and accurately. This system also will ensure that each sample is unique and will not be confused with any other sample. The Station Designation Scheme does not apply to historical data.

The first part of the sample ID will represent the area of the Site (facility/site association) where the sample was collected. It will be comprised of two components: two letters, or a letter and a number. For example, sample locations within Parcel A1 will be given a label beginning "A1", while sample locations within the Coke Oven area will be given a label beginning with "CO". See **Table 5-1** for all location designations.

The next three numerals designate the sample location number (sequential station number).

The next two letters will represent the matrix and method of collection (station type/purpose). These will be designated as SB for Soil Boring, PZ for Piezometer, or MW for Monitoring Well.

The final set of numbers will indicate the depth at which the sample was collected. In some cases, a letter may be used to indicate a relative depth (e.g.-"S" for "shallow"). Letters may also be added after the depth indicator to signify a sample the laboratory will use as a Matrix Spike (MS) or Matrix Spike Duplicate (MSD).

Each part of the sample ID for a location will be separated by a dash. For example, a sample ID of A1-001-SB-05 would designate the soil sample was collected from a soil boring at Location 001 in Parcel A1 at a depth of five feet bgs, and A1-001-PZ-15 would designate the groundwater sample was collected from a piezometer at Location Number 1 in Parcel A1at a depth of 15 feet bgs.

4 GIS FUNCTIONALITY

The GIS software implemented will be ArcMap Version 10.2.2. This GIS software runs on a PC.

ArcMap will be used for the development of data and the overall management of spatial information. All GPS coordinates and other location information associated with collected

samples—both upcoming samples and historical samples—will be incorporated in GIS so as to display the locations of all data collected. The end functionality will involve an interactive link between laboratory results and the geographic location at which they were connected. The client will be able to click on a station location and choose to view the associated lab results, reports, and other pertinent documents.

4.1. File Formats and Spatial References

GIS map documents (.mxd files) consist of a variety of shapefile and raster layer data. All files are stored in appropriate folders based on their relevant parcel(s). The spatial reference information (coordinate system, datum, etc.) used to display all data are below:

- Coordinate System: US State Plane 1983
- Zone: Maryland
- Datum: NAD 1983
- Coordinate Units: US Survey Feet

Table 5-1
Station/Sample Designation Scheme

First Segment		Second Segment	Third Segment
Facility/Site Association	**Sequential Station Number**	**Station Type/Purpose**	**Sample Depth (if applicable)**
A(A/N)-	**NNN-**	**AA-**	**NNN**

Notes: "A"= alphabetic "N"= numeric

Facility/Site Association:		Station Type/Purpose:
A1 = Parcel A1	CO = Coke Oven	PZ = Piezometer
A2 = Parcel A2	CP = Coke Point	MW = Monitoring Well
A3 = Parcel A3	TM = Tin Mill Canal	SB = Soil Boring
A4 = Parcel A4	FM = Finishing Mill	GB = Geotechnical Boring
A5 = Parcel A5	GL = Greys Landfill	SW = Surface Water Sample Location
A6 = Parcel A6	HI = Humphrey Impoundment	SD = Sediment Sample Location
A7 = Parcel A7	CC = Continuous Caster	
A8 = Parcel A8	HS = Hot Strip Mill	
A9 = Parcel A9	SY = Shipyard	
A10 = Parcel A10	BF = Blast Furnace	
B1 = Parcel B1	OH = Open Hearth	
B2 = Parcel B2	RW = Rod & Wire Mill	
B3 = Parcel B3	PR = Primary Rolling Mill	
B4 = Parcel B4	SW = Site Wide	
B5 = Parcel B5	GN = General, Non-Designated Areas	
B6 = Parcel B6	SL = Shoreline Transect	
B7 = Parcel B7	RF = Reference Transect	
B8 = Parcel B8		
B9 = Parcel B9		
B10 = Parcel B10		

Example:

A1-018-SB-02 = Soil Boring location 18 in Parcel A1, collected 2 feet bgs

APPENDIX D

Project Assessment Forms

APPENDIX E

Field Equipment Manuals

(manuals provided in electronic attachment)

Appendix E Table of Contents

Solinst Product Interface Meter Model 122 ..... Electronic
Solinst Tag Line Model 103 ..... Electronic
Solinst Water Level Meter Model 101 ..... Electronic
Solinst Water Level Meter Model 102 ..... Electronic
Summa Canisters ..... Electronic
Telescopic Jar Sampler 7300 Series ..... Electronic
Trimble Geo 7 Series ..... Electronic
Trimble GPS Pathfinder ProXRT Receiver ..... Electronic
Trimble Pro Series Receivers ..... Electronic
Wildlife Supply Company Petite Ponar Grab ..... Electronic
Wildlife Supply Company Standard Ponar Grab ..... Electronic
YSI ProPlus ..... Electronic

APPENDIX F

Laboratory Quality Assurance Manuals

(manuals provided in electronic attachment)

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