November 2019

Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS Sampling

Quality Assurance Project Plan

Prepared for Wisconsin Department of Natural Resources and U.S. Environmental Protection Agency
Great Lakes National Program Office
EPA GLRI Grant No. GL-00E02392

November 2019
Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS Sampling

Quality Assurance Project Plan

Prepared for
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ABBREVIATIONS

%R	percent recovery
ASTM	ASTM International
BUI	Beneficial Use Impairment
CEC	Coleman Engineering Company
COC	contaminant of concern
CT	CT Laboratories
DNR	Wisconsin Department of Natural Resources
DQO	data quality objective
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
ETA	Eurofins TestAmerica
FFS	*Menomonee and Milwaukee Rivers Focused Feasibility Study*
FSM	Field Safety Manager
FSP	Field Sampling Plan
FTL	Field Team Leader
GEL	GEL Laboratories
GLLA	Great Lakes Legacy Act
GLNPO	Great Lakes National Program Office
GLRI	Great Lakes Restoration Initiative
GLWQA	Great Lakes Water Quality Agreement
GPS	global positioning system
IGLD85	International Great Lakes Datum of 1985
KK	Kinnickinnic
LCS	laboratory control sample
LDC	Laboratory Data Consultants
LWD	low water datum
MD	matrix duplicate
MDEQ	Michigan Department of Environmental Quality
MDL	method detection limit
MGP	Manufactured Gas Plant

MKE AOC	Milwaukee Area of Concern
Mudpuppy	*R/V Mudpuppy II*
MRL	method reporting limit
MS	matrix spike
MSD	matrix spike duplicate
NIST	National Institute of Standards and Technology
OU1	Operable Unit 1
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PFAS	perfluoroalkyl and polyfluoroalkyl substances
Project	Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS Sampling
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RAP	*Milwaukee Estuary Stage 1 Remedial Action Plan*
RPD	relative percent difference
SEDD	Staged Electronic Data Deliverable
Sigma	The Sigma Group
SIR	Site Investigation Report
Site	MKE AOC
SMC	South Menomonee Canal
SOP	Standard Operating Procedure
SSP	Site Safety Plan
TOC	total organic carbon
TSS	total suspended solids
UWM	University of Wisconsin – Milwaukee
WSLH	Wisconsin State Laboratory of Hygiene

1 Introduction

1.1 Title of Plan and Approval (Approval for Field Implementation)

Quality Assurance Project Plan
Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS
Milwaukee, Wisconsin

Prepared by

Anchor QEA, LLC
290 Elwood Davis Road, Suite 340
Liverpool, New York 13088

Approved by: Scott Inman Date: December 6 2019
Scott Inman, DNR Project Manager

Approved by: Donalea Dinsmore Date: 8 November 2019
Donalea Dinsmore, DNR Quality Assurance Lead

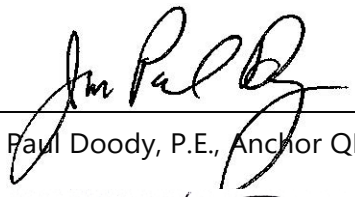
Approved by: HEATHER WILLIAMS Digitally signed by HEATHER WILLIAMS Date: 2019.12.06 09:24:52 -06'00' Date:
Heather Williams, EPA Sediment Task Force Lead

Approved by: N/A Date:
Kristen Isom, EPA GLNPO Secondary Contact

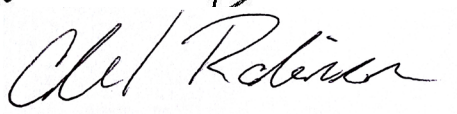
Approved by: Mark J. Loomis Digitally signed by Loomis, Mark Date: 2019.12.06 09:05:04 -06'00' Date:
Mark Loomis, EPA QA Manager

Approved by:  Date: November 1, 2019

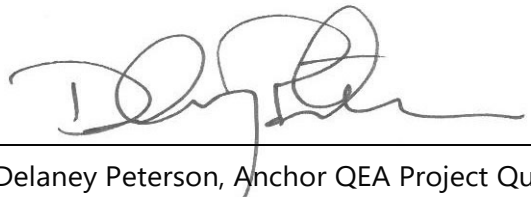
Kim Powell, P.E., Anchor QEA Project Manager

Approved by:  Date: November 1, 2019

Paul Doody, P.E., Anchor QEA Project Engineer

Approved by:  Date: November 1, 2019

Chad Robinson, Anchor QEA Field Team Leader

Approved by:  Date: November 1, 2019

Delaney Peterson, Anchor QEA Project Quality Control Manager

1.2 Introduction

This *Quality Assurance Project Plan* (QAPP) has been prepared by Anchor QEA, LLC, on behalf of the Wisconsin Department of Natural Resources (DNR) to accomplish the objectives of a multi-year U.S. Environmental Protection Agency (EPA) Great Lakes Restoration Initiative (GLRI) grant (EPA GLRI Grant No. GL-00E02392). Under this Contract, Anchor QEA will collect field data to characterize sediments within the South Menomonee Canal (SMC) Investigation Area and screen sediments for perfluoroalkyl and polyfluoroalkyl substances (PFAS) in the Milwaukee Area of Concern (MKE AOC) (Project, Site) located in Milwaukee, Wisconsin (Figure 1). This QAPP's objectives include both those of the EPA AOC program and requirements in Wisconsin Administrative Code Chapter NR 716 (Site Investigations). This QAPP and associated work will be implemented under the Great Lakes Legacy Act (GLLA) and will follow the requirements from the Wisconsin Administrative Code Chapter NR 700.

The EPA requires that all environmental monitoring and measurement efforts mandated or supported by EPA (including under GLLA) participate in a centrally managed quality assurance (QA) and quality control (QC) program. Any party generating data under this program is responsible for implementing minimum procedures to confirm that the precision, accuracy, completeness, and representativeness of its data are known and documented. To be certain the responsibility is met uniformly, each party must prepare a written QAPP covering each project it is to perform.

1.3 Document Organization

This document format is generally consistent with the *EPA Guidance for Quality Assurance Project Plans* (QA/G-5) (EPA 2002) and the *EPA Requirements for Quality Assurance Project Plan*s (QA/R-5) (EPA 2001). QAPPs are approved by Anchor QEA's Project Manager, Project Engineer, Project QC Manager, and Field Team Leader and are submitted to the DNR and EPA Great Lakes National Program Office (GLNPO) for approval before field data collection begins. As detailed in the guidance, this QAPP is organized into the following four sections:

- Section 1 (Introduction) introduces the Project, distribution list, and document approvals.
- Section 2 (Project Management) covers aspects of project management, objectives, and background information; identifies the roles and responsibilities of Project personnel; defines the lines of communication; and identifies the objectives and technical approach to achieving the goals at the Site.
- Section 3 (Data Generation and Acquisition) describes the design and implementation of measurement systems that will be used during the field investigation at the Site, and laboratory-based testing, as well as the sampling procedures, analytical methods, and data handling and documentation procedures. These elements are described further in the Field Sampling Plan (FSP; Anchor QEA 2019a). The Standard Operating Procedures (SOPs) for field sampling are included in the FSP (SOP 01 – Field Records; SOP 02 – Navigation and Boat Positioning; SOP 03 – Sediment Sampling; SOP 04 – Sediment Core Processing; SOP 05 –

Water Sampling; SOP 06 – Sample Custody; SOP 07 – Sample Handing, Packaging and Shipping; SOP 08 – Equipment Cleaning/Decontamination; and SOP 09 – Investigation-Derived Waste Handling and Disposal). SOPs for laboratory analyses are presented in Attachment A of this QAPP. QC procedures, frequency requirements, acceptance criteria, and corrective action procedures are also provided in this section.

- Section 4 (Assessment and Oversight) describes the measures used to implement the QAPP and the procedures outlined in Section 3.
- Section 5 (Data Validation and Usability) describes the QA activities, including data validation and usability assessments, that are expected to occur after the data collection and assessment phase is completed for this Project.
- Section 6 provides a list of the references cited in this QAPP.

1.4 Distribution List

The key Project personnel are provided in Figure 2 and a distribution and contact list is included as Table 1.

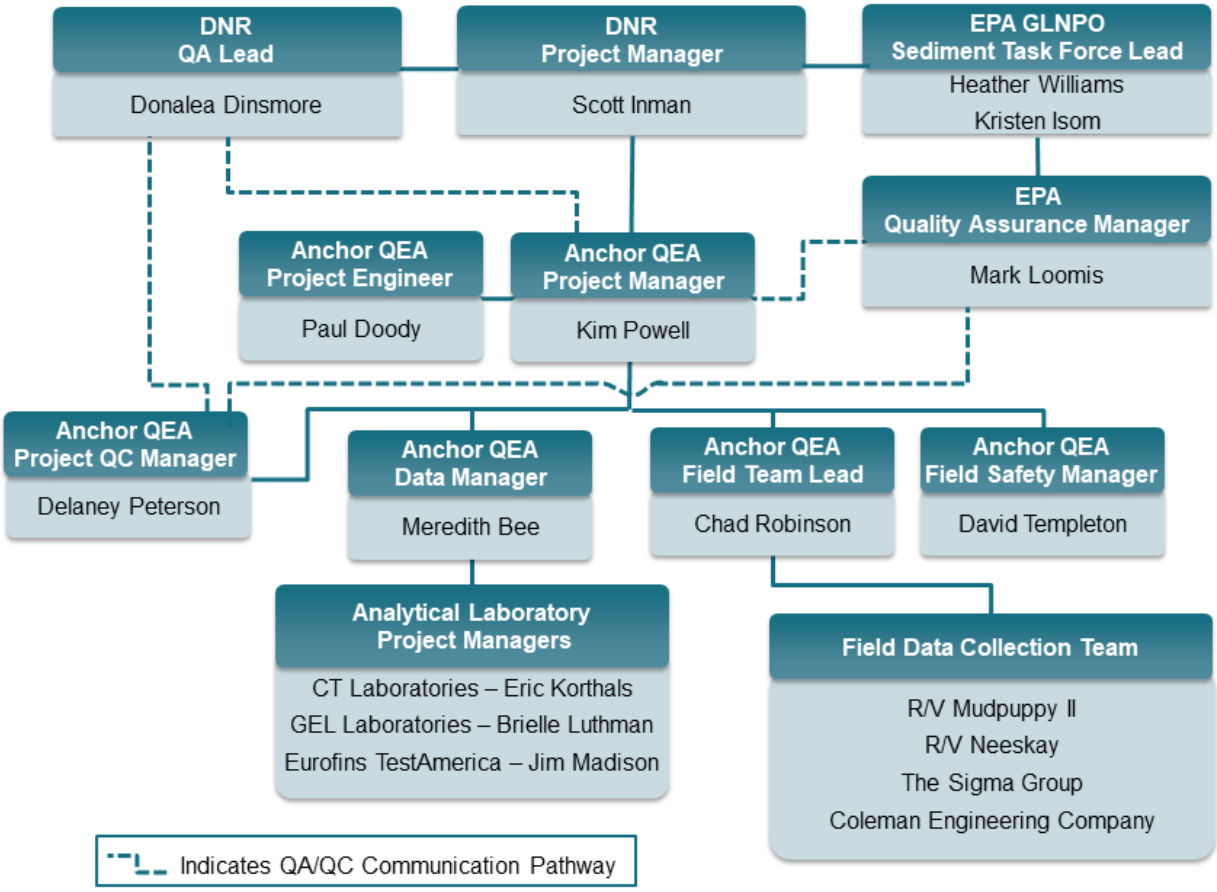


Figure 2
Project Organization Chart

2 Project Management

2.1 Project Organization and Responsibilities

This section outlines the personnel involved in the team organization. The management structure provides for direct and constant operational responsibility, clear lines of authority, and the integration of QA activities. QA functions are explained in the following subsections. Anchor QEA is responsible for planning, conducting, and overseeing work for this Project. A Project organizational chart presenting key Anchor QEA Project personnel and chain of command is presented in Figure 2.

2.1.1 Project Management

DNR Project Manager—Mr. Scott Inman is the DNR Project Manager for this Project. As DNR Project Manager, Mr. Inman is the primary DNR contact and is responsible for overall contract management of this Project. In addition, all corrective actions will be reported to Mr. Inman, who will be responsible for approving any corrective actions. The DNR Project Manager is responsible for reviewing and approval of this QAPP.

DNR Secondary Contacts—Mr. Chris Dietrich and Mr. Brennan Dow are the DNR Secondary Contacts for this Project. As DNR Secondary Contacts, Mr. Dietrich and Mr. Dow are responsible for supporting the DNR Project Manager and this Project.

EPA GLNPO Sediment Task Force Lead—Ms. Heather Williams is the EPA GLNPO Sediment Task Force Lead for this Project. As EPA Sediment Task Force Lead, Ms. Williams is the primary EPA contact for GLNPO and is responsible for all stages of this Project. The EPA GLNPO Sediment Task Force Lead is responsible for reviewing and approval of this QAPP.

EPA GLNPO Secondary Contact—Ms. Kristen Isom is the EPA GLNPO Secondary Contact for this Project. As EPA GLNPO Secondary Contact, Ms. Isom is responsible for supporting the EPA GLNPO Sediment Task Force Lead and this Project, and is responsible for reviewing and approving this QAPP.

Anchor QEA Project Manager—Ms. Kim Powell, P.E. is Anchor QEA Project Manager. Anchor QEA Project Manager is responsible for reviewing, approving, and implementing the QAPP, distributing copies of the QAPP, maintaining the official approved QAPP, scheduling, personnel management, document preparation, document and data review, communication with DNR, EPA, and contractors, and Anchor QEA budgeting. The Anchor QEA Project Manager will coordinate with the DNR Project Manager, EPA GLNPO Project Managers, and other Anchor QEA staff or subcontractors (as appropriate). The Anchor QEA Project Manager will be the primary point of contact and control for matters concerning the Project.

Anchor QEA Project Engineer—Mr. Paul Doody, P.E. is the Anchor QEA Project Engineer. The Anchor QEA Project Engineer is responsible for reviewing, approving, and overseeing implementation of the QAPP. The Anchor QEA Project Engineer will coordinate with the Anchor QEA Project Manager and will serve as the secondary point of contact and control for matters concerning the Project.

Anchor QEA Data Manager—The Anchor QEA Data Manager, Ms. Meredith Bee, is responsible for the coordination of computerized data management activities and communication with laboratory personnel. Her responsibilities include the following:

- Manage, maintain, and input a record of all samples collected and the sample identification information of each sample collected.
- Manage and maintain a record of all samples submitted to the laboratory, analyses being performed, analytical results and reports, and data validation reports.
- Prepare data reduction and review data outputs to support data evaluation, assessment, and reporting.
- Initiate and schedule the laboratory analysis with the following: CT Laboratories (CT) in Baraboo, Wisconsin; GEL Laboratories (GEL) in Charleston, South Carolina; Eurofins TestAmerica (ETA) in Burlington, Vermont, and Wisconsin State Laboratory of Hygiene (WSLH) in Madison, Wisconsin.

Analytical Chemistry Laboratory Project Managers—Eric Korthals of CT, Brielle Luthman of GEL, Jim Madison of ETA, and Graham Anderson of WSLH will serve as the Laboratory Project Managers. The Laboratory Project Managers will review and implement this QAPP, oversee the analysis of samples, oversee data compliance with the requirements of this QAPP, and communicate with Anchor QEA Field Team Leader (FTL) and Anchor QEA Project QC Manager, as appropriate.

2.1.2 Quality Assurance

EPA QA Manager—Mr. Mark Loomis will be responsible for review and approval of this QAPP. Mr. Loomis will communicate with Anchor QEA Project Manager on QA/QC-related concerns. The EPA QA Manager will also have the discretion to conduct external performance and system audits of field and laboratory activities. The EPA QA Manager will serve as the point of contact for Anchor QEA Project QC Manager on any data management and validation-related activities. Mr. Loomis will communicate with Anchor QEA Project QC Manager on the upload of data to the Great Lakes Sediment Database.

DNR QA Lead—Ms. Donalea Dinsmore will be responsible for review and approval of this QAPP regarding the requirements of the Wisconsin Administrative Code. Ms. Dinsmore will communicate with Anchor QEA Project Manager on QA/QC-related concerns and will serve as the point of contact for Anchor QEA Project QC Manager on any data management and validation-related activities.

Anchor QEA Project QC Manager—To provide QC oversight, Ms. Delaney Peterson will serve as Anchor QEA Project QC Manager for this Project. The Anchor QEA Project QC Manager is responsible for implementing and administering the Anchor QEA QA/QC Program as it relates to the Project. The Anchor QEA Project QC Manager is responsible for reviewing, updating, and implementing the QAPP, coordinating all procedures and tasks pertaining to QA, including correspondence with the laboratories listed above on issues relating to data quality, and reporting to the EPA QA Manager and Anchor QEA Project Manager on QA issues. The Anchor QEA QC Manager will serve as the point of contact for the EPA QA Manager on quality-related matters. The Anchor QEA Project QC Manager is also responsible for validation oversight and review of data following validation to determine its usability for decision-making and reporting activities. Data review and QC will be supported by additional qualified Anchor QEA staff.

2.1.3 Field Team

Anchor QEA Field Team Leader—Mr. Chad Robinson is Anchor QEA FTL for this Project. He will serve as the field activities coordinator for Anchor QEA on-Site activities and will be responsible for the daily direction of the team members (Project field personnel) regarding FSP-specific tasks and the requirements outlined in this QAPP. Mr. Robinson is responsible for reviewing and approving this QAPP. Mr. Robinson will coordinate with EPA's sampling vessel, the *R/V Mudpuppy II* (Mudpuppy) and the University of Wisconsin – Milwaukee's (UWM's) research vessel, *R/V Neeskay*, who will be collecting sediment cores within the SMC and the MKE AOC respectively. Mr. Robinson will also coordinate with Coleman Engineering Company (CEC), The Sigma Group (Sigma), CT, GEL, and ETA, for sample bottle deliveries and sample shipments with the laboratories. Additional responsibilities include providing training to the sample collection field staff; providing the initial technical review of deliverables and data collection activities; monitoring QC activities and responding to deficiencies identified in the field; collecting and storing original field documentation; maintaining sampling equipment in a secure location; and overseeing field survey and sample collection tasks.

Anchor QEA Field Safety Manager—Mr. David Templeton will be Anchor QEA Field Safety Manager (FSM), responsible for implementing the Site Safety Plan (SSP). Anchor QEA FSM will perform safety and health monitoring and support compliance with safety and health requirements, including those in Anchor QEA Project-specific SSP (Anchor QEA 2019b).

2.1.4 Analytical Laboratories

CT will serve as the analytical laboratory for sediment chemical analyses and will analyze samples for metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and total organic carbon (TOC). GEL will serve as the analytical laboratory for PFAS analyses in sediment and water, TOC analyses in associated sediment samples, and total suspended solids (TSS) in associated water samples. ETA will conduct the geotechnical analyses, including moisture content, specific gravity,

particle size, and Atterberg limits. WSLH will serve as the analytical laboratory for phosphorus sediment and surface water sampling. Data validation will be conducted by Laboratory Data Consultants (LDC) or internally by Anchor QEA staff. The Laboratory Project Managers will oversee the analyses of samples and will serve as points of contact for the Anchor QEA Project QC Manager. The Anchor QEA Project QC Manager will correspond with the laboratory on any analytical and data quality issues. The Anchor QEA Data Manager will coordinate with the laboratory regarding electronic data deliverables (EDD). The analytical methods and reporting limits for sediment and water samples are summarized in Tables 2 and 3.

2.1.5 Data Validation

Chemistry data validation will include completeness and compliance checks, data assessment, and Stage 2A and 2B validations following *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use* (EPA 2009), in conjunction with the EPA Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review (EPA 2017a, 2017b) to assess compliance with the FSP (Anchor QEA 2019a) and this QAPP. Geotechnical data will be reviewed for completeness and usability by Anchor QEA.

Data will be validated by LDC. The Anchor QEA Project QC Manager is responsible for coordination and tracking of the documents submitted to the data validator and will act as the liaison between the laboratory and data validator on issues regarding analysis and data quality.

2.2 Background Information/Problem Definition

2.2.1 Site Description

The MKE AOC is one of five Great Lakes Areas of Concern in Wisconsin. It comprises portions of three rivers—Milwaukee, Menomonee, and Kinnickinnic (KK)—and the Inner Harbor, Outer Harbor, and nearshore areas of Lake Michigan, bounded by a line extending north from Sheridan Park to the City of Milwaukee's Linwood water intake. The MKE AOC was initially listed in 1987 under the Great Lakes Water Quality Agreement (GLWQA). This AOC was later expanded in 2008 to include legacy contaminated sediments in the Little Menomonee River located in the upper portion of the Menomonee River, along with Lincoln Creek and Cedar Creek located in the upper portion of the Milwaukee River. The lower estuary portion of MKE AOC is depicted in Figure 1.

Though the MKE AOC contains multiple rivers and reaches, the site and the work described herein includes the following areas of interest:

- SMC Investigation Area
  - SMC
  - Burnham Canal

- MKE AOC PFAS Investigation Areas:
  - Milwaukee River downstream (Milwaukee River Reach 4)
  - Operable Unit 1 (OU1) of the Menomonee and Milwaukee rivers (Menomonee River Reaches 4 and 5), along with SMC
  - KK River downstream (KK River Reaches 2 and 3), along SkipperBud's slip
  - Outer Harbor
  - Lake Michigan outside of the breakwater

The SMC Investigation Area encompasses approximately 17 acres of surface area and 0.9 river miles, from the headwater of the canal to the confluence with the Menomonee River. This area is part of the Inner Harbor and includes a federal navigation channel. The federal navigation channel within the SMC is authorized to 21 feet below the low water datum (LWD) of 577.5 feet (International Great Lakes Datum of 1985 [IGLD85]). According to the Scope of Work, the future of the federal navigation channel within the SMC is uncertain and may remain as is, be deauthorized, or be reauthorized to a depth for current marine vessel use, such as 16 feet below the LWD (577.5 feet IGLD85) (DNR 2019). The SMC Investigation Area also includes 0.6 acre of the Burnham Canal downstream of the currently inoperative Canadian Pacific Railway Burnham swing bridge. In total, this SMC Investigation Area is approximately 17.6 acres.

The MKE AOC PFAS Investigation Area consists of five discrete areas: Milwaukee River Reach 4; Menomonee River Reaches 4 and 5; KK River Reaches 2 and 3; the Outer Harbor; and Lake Michigan outside of the breakwater. These areas have been identified to provide a general characterization of PFAS within the MKE AOC.

The Milwaukee River downstream area is herein referred to as Milwaukee River Reach 4. Milwaukee River Reach 4 is approximately 2.3 miles long, beginning at the former North Avenue Dam and continuing to the Menomonee River confluence. The river passes through downtown Milwaukee, with shoreline consisting primarily of sheetpile bulkheads, and includes 17 bridge crossings. The banks are urbanized with a mix of residential and commercial properties.

OU1 of the Menomonee and Milwaukee rivers (described in *Menomonee and Milwaukee Rivers Focused Feasibility Study* [FFS; CH2M 2019]) consists of 1.9 river miles on the Menomonee River from the West Canal Street Bridge to the confluence with the Milwaukee River. This area includes Menomonee River Reaches 4 and 5. Menomonee River Reach 4 extends from the 25th Street Bridge to the 16th Street Bridge. The Former West Side Manufactured Gas Plant (MGP [Bureau for Remediation and Redevelopment Tracking System No. 02-41-556251]) is located immediately downstream of the 25th Street Bridge. Menomonee River Reach 5 begins at the 16th Street Bridge and extends 1 mile downstream to the confluence with the Milwaukee River. This portion of the river

consists of mixed industrial and commercial use. The shoreline is mostly sheetpile bulkhead walls and a few portions of concrete bulkhead.

The KK River downstream of Becher Street to the mooring basin encompasses KK River Reaches 2 and 3. KK River Reach 2 is defined as Becher Street Bridge downstream to the South Kinnickinnic Bridge. KK River Reach 2 is a mixture of industrial and commercial use. The shoreline consists mostly of sheetpile bulkhead walls with some docks, piers, and slips. Water depths in Reach 2 range from 2 to 19 feet. KK River Reach 3 is defined as the KK River immediately downstream of the South Kinnickinnic Street Bridge to the end of the Municipal Mooring Basin (Turning Basin). KK River Reach 3 also includes the SkipperBud's slip and the navigation channel. KK River Reach 3 is a mixture of industrial and commercial uses. The shoreline is primarily sheetpile bulkhead wall with portions of natural shoreline at the SkipperBud's slip. Water depths in Reach 3 range from 12 to 27 feet.

The Outer Harbor includes the area from the confluence of the KK River and Milwaukee River at the Daniel Hoan Memorial Bridge out to the boundaries of the breakwater. This portion of the harbor includes industrial, commercial, and public park space. The shoreline consists of a mix of sheetpile bulkhead wall, concrete bulkhead, armor stone revetment, and sand beach. Water depths in the Outer Harbor range from approximately 7 to 32 feet.

Lake Michigan immediately outside of the breakwater is open lake, with water depths ranging from 30 to 50 feet near the harbor. The breakwater consists of sheetpile bulkhead wall, armor stone revetment, and concrete bulkhead. The navigation channel is maintained approximately 500 feet east of the harbor entrance.

2.2.2 Site History

Under the GLWQA, the DNR completed the *Milwaukee Estuary Stage 1 Remedial Action Plan* (RAP) in 1991 (DNR 1991). Updates to the RAP have been periodically performed, with the most recent update in December 2017 (DNR 2017). The RAP identifies the project areas as requiring additional sediment characterization.

Historical sampling in the MKE AOC has identified various contaminants of concern (COCs), including metals, PCBs, and PAHs resulting from historical industrial discharge. There are multiple Superfund sites, GLLA sites, and other known contaminated sites within the MKE AOC. A summary of known contaminated sites within the MKE AOC and their status is provided in Table 4.

Table 4
Known Contaminated Sites within MKE AOC

Location	Status	Superfund	GLLA
Burnham Canal Superfund Site	Design in progress	X	
Cedar Creek Superfund Site	In progress	X	
Moss-American Superfund Site	RA complete	X	
Solvay Coke Superfund Alternative Sites	Investigation underway	X	
Estabrook Park	RA complete		X
Lincoln Park and Milwaukee River Channels Phases 1 and 2	RA complete		X
Milwaukee River Reach 4	Investigation complete		X
KK River	RA complete		X
Inner Harbor	Assessment needed		X
Former MGP Menomonee River (Energies West Side)	FFS complete		X
Former MGP Milwaukee River (Energies Third Ward)	FFS complete		X
Milwaukee Die Cast Facility Discharge	Assessment needed		

Notes:
Source: CH2M 2019
FFS: Focused Feasibility Study
RA: Remedial Action

Within the RAP, EPA identified existing Beneficial Use Impairments (BUIs) for the MKE AOC (DNR 2017), as summarized in Table 5. Of the 11 BUIs, 10 are listed as impaired and 7 are linked to contaminated sediment in the MKE AOC. Additional data collection described in this FSP will supplement the historical and ongoing data characterization efforts in the overall MKE AOC. The ultimate goal is the removal of BUIs, which is expected to include remediation of the contaminated sediments identified through these data characterization efforts.

Table 5
Status of Beneficial Use Impairments in the MKE AOC

Beneficial Use Impairment	Status	Linked to Contaminated Sediment
Fish tumors or other deformities	Impaired	X
Bird or animal deformities or reproductive problems	Suspected	X
Restriction on fish and wildlife consumption	Impaired	X
Restrictions on dredging activities	Impaired	X
Degradation of benthos	Impaired	X
Degradation of phytoplankton and zooplankton populations	Impaired	

Beneficial Use Impairment	Status	Linked to Contaminated Sediment
Loss of fish and wildlife habitat	Impaired	X
Degradation of fish and wildlife populations	Impaired	X
Beach closings	Impaired	
Eutrophication or undesirable algae	Impaired	
Degradation of aesthetics	Impaired	

Notes:
"X" indicates BUIs are linked to contaminated sediment.
BUI: Beneficial Use Impairment

2.2.3 Project Objectives

The primary objectives for the Project identified in the FSP are as follows:

- Objective 1: Characterize the chemical and physical properties of sediments within the SMC Investigation Area.
- Objective 2: Determine prevalence and distribution of PFAS within sediments and surface water across the Milwaukee River Estuary MKE AOC. This is a screening-level investigation to identify areas that may require further investigation and/or remedial action, if warranted and appropriate.

The MKE AOC has historical pollution and a history of ecological degradation. Objectives 1 and 2 will identify the extent of contamination and whether further Feasibility Studies and Remedial Action are warranted. By obtaining the data necessary to evaluate the degree and extent of sediment contamination, areas of further investigation and remedial alternatives can be identified. The Site is shown in Figure 1.

2.3 Project Description and Schedule

Field activities are described in detail in the FSP and are summarized in the following subsections.

2.3.1 Sample Collection

Field sampling will occur as described in the FSP (Anchor QEA 2019a), which includes figures and tables of proposed sample locations and SOPs for sample collection and processing. Substantive deviations from the SOPs will be recorded in the Daily Log or field logbook and on a Field Deviation Form, as well as reported to the Anchor QEA Project Manager before the deviations take place. In addition, the DNR and EPA will be notified of any substantive changes as soon as possible.

2.3.2 Field Methods and Decontamination Procedures

Field methods for sample collection, handling, and documentation, as well as equipment decontamination procedures, are outlined in detail in the FSP and in the field SOPs (Anchor QEA 2019a).

2.3.3 Analytical Procedures

Details regarding sample documentation and delivery to the analytical laboratories are included in the FSP and field SOPs (Anchor QEA 2019a). Laboratory analyses for the Project will be performed by the laboratories as described in Section 2.1.4 of this QAPP.

Laboratory data will be of known and documented quality as specified by the applicable EPA guidance documents. Laboratory data will be compliant with EPA quality requirements, which require data to withstand independent review and confirmation.

There will be no deviation from the EPA-approved methods unless approved by the DNR and EPA GLNPO Sediment Task Force Lead, and QA Manager. If requested, Anchor QEA will draft Project-specific improvements or modifications to the EPA methods in coordination with the analytical laboratories.

Anchor QEA will be responsible for resolving data discrepancies with the laboratories and will inform the DNR Project Manager, EPA GLNPO Sediment Task Force Lead, and QA Manager of issues or delays.

2.3.4 Schedule

The field tasks identified in the FSP and this QAPP will be conducted in November 2019, beginning the week of November 4, 2019, and conclude November 15, 2019. The following is the anticipated schedule for field work and reporting:

- November 4, 2019 – SMC investigation begins (estimate 5 days)
- November 11, 2019 – MKE AOC PFAS Investigation and phosphorus sampling begins (estimate 5 days)
- November 15, 2019 – Field sampling completed (weather pending)
- December 31, 2019 – Preliminary laboratory data received
- January 29, 2020 – Data Usability Memorandum submitted
- February 4 – 2020 – 50% SIR submitted (90% SIR submitted 30 days after receipt of comments)
- February 28, 2020 – Draft PFAS Special Study Report submitted (Final PFAS Special Study Report submitted 30 days after receipt of comments)

This schedule is subject to change based on weather delays, permits, and other factors that are out of the project personnel's control.

2.4 Data Quality Objectives and Criteria for Measurement Data

The overall objective of this Project is to provide data of known and documented quality to ensure that the Project objectives described in the FSP (Anchor QEA 2019a) are met.

2.4.1 Data Quality Objectives

Data quality objectives (DQOs) provide a qualitative and quantitative framework and series of planning steps based on the scientific method around which data collection programs can be designed. The use of DQOs ensures the following:

- The objectives of the investigation are clearly defined.
- The type, quantity, and quality of environmental data used in decision-making are appropriate for their intended application.
- Acceptable levels of decision error and performance goals are specified, such that the quantity and quality of data needed to support management decisions are provided.

The DQO process consists of the following seven steps (EPA 2006), which are used during the planning of the site assessment process to validate the field activities and data collection operations, and to demonstrate that resulting data meet the Project objectives:

1. State the problem.
2. Identify the goal of the study.
3. Identify the information inputs.
4. Define the boundaries of the study.
5. Develop the analytic approach.
6. Specify performance or acceptance criteria.
7. Develop the plan for obtaining data.

Following these seven steps supports the Project plan being carefully thought out and the data collected providing sufficient information to support the key decisions that must be made. Table 6 (Data Quality Objectives) summarizes the application of the DQO process to the site characterization for the Project.

2.4.2 Criteria for Measurement Data

The quality of the laboratory data is assessed by precision, accuracy, sensitivity, completeness, representativeness, and comparability. Definitions of these parameters and the applicable QC procedures are given in the following sections. Applicable quantitative goals for these data quality parameters are listed in Table 7.

2.4.3 Precision

Precision describes the reproducibility of measurements of the same parameter for a sample under the same or similar conditions. Specifically, it is a quantitative measure of the degree of variability of a group of measurements compared to the average value. Precision is evaluated most directly by recording and comparing multiple measurements of the same parameter made on the same sample under similar conditions. Standard deviation, coefficient of variation, range, and relative range are terms often used to express precision.

Precision is determined in the laboratory by assessing the relative percent difference (RPD) for sample duplicate and matrix spike (MS)/matrix spike duplicate (MSD) pairs, as shown in the following equation:

RPD= 100% x (sample result – duplicate result) / ((sample result + duplicate result)/2)

Precision measurements can be affected by the nearness of a chemical concentration to the method reporting limit (MRL), and RPD values may be erroneously inflated in these instances. Parent and/or duplicate results that are less than five times the MRL will be evaluated by using the difference between the results and using a control limit of plus or minus two times the MRL for solid matrices or of plus or minus the MRL for aqueous matrices.

Field precision—Field precision will be assessed through the collection and analysis of field duplicates and MS/MSD sample aliquots. Field duplicates and MS/MSDs will be collected at a rate of 5%. Each field duplicate sample will be collected for the suite of chemical analyses designated for the original sample. The analytical DQO for field precision is plus or minus 50% RPD.

Laboratory precision—Precision in the laboratory will be assessed using laboratory duplicates and MS/MSD results. Analytical DQOs for laboratory precision are presented in Table 7.

2.4.4 Accuracy

Accuracy is the comparison between experimental and known or calculated values, expressed as a percent recovery (%R), and measures the bias of a measurement system. Variations in accuracy result from a combination of random error (precision) and systematic error (bias), which are due to sampling and analytical operations. Sources of error include the sampling process, field contamination, preservation, handling, sample matrix, sample preparation, and analytical techniques.

Accuracy will be assessed at the laboratory through the analysis of laboratory control samples (LCSs), MS/MSDs, and surrogate spikes as appropriate to each method. The %R is derived from analysis of standards spiked into deionized water (the LCS), or into actual samples (MS or surrogate spike).

LCS and surrogate %R are calculated as follows:

$$\%R = 100\% \times (\text{measured value} / \text{true value})$$

MS/MSD %R is calculated using the following equation:

$$\%R = 100\% \times (\text{observed spiked sample concentration} - \text{unspiked sample concentration}) / \text{true concentration of spike}$$

One field sample in every twenty will be marked as an MS/MSD sample and extra sample mass or volume will be collected as needed. The level of recovery of an analyte in MS/MSD samples is dependent on the sample matrix, the method of analysis, and native concentrations. The concentration of the analyte relative to the detection limit of the method is also a factor. MS/MSD samples and surrogate spikes will be used to evaluate the effect of the sample matrix on the accuracy of the analytical data. Analytical DQOs for LCS and MS %R are presented in Table 7. Analytical QC sample frequencies are presented in Table 8.

2.4.5 Sensitivity

Sensitivity is the ability of the method or instrument to detect the constituent of concern or other required data at the level of interest. Sensitivity is typically expressed in the form of method detection limits (MDLs) and MRLs.

- The MDL is the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is distinguishable from method blank results. The MDL is determined from the replicate analyses of matrix spiked at a known and low-level concentration and evaluation of routine method blanks.
- The MRL is the minimum level of an analyte that can be reported with a specified degree of confidence. These values are adjusted for percent moisture, dilutions, and sample size on an individual sample basis.

Tables 2 and 3 present the target analyte MDLs and MRLs for the specified analyses.

Detected results reported between the laboratory MDLs and MRLs will be J-qualified as estimated. Undetected results will be reported at the sample-specific MDL, adjusted for percent moisture, dilution, and sample aliquot size.

2.4.6 Completeness

Completeness is a measure of the amount of data that is determined to be valid in proportion to the amount of data collected. Completeness will be calculated as follows:

$$C = \frac{(Number\ of\ acceptable\ data\ points)\ x\ 100}{Total\ number\ of\ data\ points}$$

The completeness goal for all components of this Project is 95%. Data that have been qualified as estimated because the QC criteria were not met will be considered valid for the purpose of assessing completeness. Data that have been rejected will not be considered valid for the purpose of assessing completeness.

2.4.7 Representativeness

Representativeness describes the degree to which sample data accurately and precisely represent a characteristic of the material being measured. Representativeness is a qualitative term that is evaluated to determine whether in situ and other field measurements are made and samples are collected in such a manner that the resulting data appropriately reflect environmental conditions. Representativeness will be established by the following procedures:

- Sampling procedures will adhere to those specified in the planning documents.
- Equipment blanks will be collected to evaluate cross-contamination.

2.4.8 Comparability

Comparability is a parameter used to express the confidence with which one set of data may be compared with another. To achieve comparability in datasets, standard techniques will be used to collect and analyze representative samples and to report analytical results. The following items enhance the comparability of datasets:

- Two datasets with the same set of variables of interest
- The same or convertible units
- Similar analytical and QA procedures
- The measurements collected at a similar time
- Similar measuring devices
- The same rules for excluding certain types of observations for both samples

To verify that data derived from this field and laboratory effort are comparable to each other and to other data produced using EPA methods or similar, these procedures will be followed:

- All samples will be submitted for analysis by equivalent analytical methods (with the same analytical parameters and similar detection/reporting limits).
- Units of measure (e.g., micrograms per liter, micrograms per kilogram) will be the same for all reporting.
- All samples will be handled and prepared in the same manner according to the field collection and core processing SOPs (Anchor QEA 2019a).

2.4.9 Quality Control

Rinsate blanks, field duplicates, and MS/MSD samples will be collected and submitted to the analytical laboratories to assist in the evaluation of the quality of data resulting from the sampling program. Field QC samples will be collected in the same manner as normal field samples. Rinsate blanks for PFAS analyses will be collected using laboratory-supplied PFAS-free water as described in SOP-05. QC samples will also be prepared and analyzed by the laboratories. Laboratory QC samples will include method blanks, LCSs, laboratory duplicates, and MS/MSDs. The QC program is described in detail in Section 3.5. Table 8 lists the frequency of field and laboratory QC sample analyses.

2.5 Special Training Requirements/Certification

For sample collection tasks, it is important that field crews and laboratory staff are trained in standardized data collection requirements so that the data collected are consistent among staff. Field crews will comprise individuals who are fully trained in the collection and processing of subsurface sediment cores, collection of surface water samples, decontamination protocols, and chain-of-custody procedures. In addition, field crews will be trained in appropriate health and safety regulations to provide employees with the knowledge and skills enabling them to perform their jobs safely and with minimum risk to their personal health.

The following subsections summarize training requirements for Anchor QEA personnel and subcontractors.

2.5.1 Field Training

Documentation—Team members will be trained in appropriate procedures for field documentation. The Anchor QEA Project QC Manager will coordinate with the Anchor QEA FTL and Anchor QEA Project Manager to ensure documentation is transferred to an Anchor QEA internal Project file folder on a real-time basis to the extent practical in an organized manner.

Sampling—Personnel operating core sampling, water quality monitoring, and surface water equipment will be trained in the operation of the equipment. Staff performing sample collection will be trained in the methods of sample collection. Staff will further review the SOPs and sign the SOP Acknowledgement Forms to certify they have read and understand the procedures prior to conducting field work. This includes the special considerations associated with PFAS sample collection procedures. Field personnel should be familiar with EPA Method 1669 'clean hands, dirty hands' sampling techniques developed for low-level metals water sample collection procedures. Since this method was developed for metals sample collection, procedures will not be followed exactly, but will be used as a guideline to prevent cross-contamination. Previous sampling experience using similar methods will be required for at least one field staff prior to working on site.

The Anchor QEA FTL will be responsible for providing training to the field staff responsible for sample collection and sample management activities and ensuring that the assigned field personnel are competent to properly conduct the sampling and document field activities in accordance with the FSP. The Anchor QEA FTL will also ensure that all staff have read and can readily reference the Michigan Department of Environmental Quality (MDEQ) General PFAS Sampling Guidance (MDEQ 2018) and EPA Method 1669. Samples will be logged by qualified personnel with experience logging sediment according to ASTM International (ASTM) Method D2487.

Global Positioning System (GPS)—The Anchor QEA team, as well as the contractor selected to assist with sample collection, will be trained in the proper use and operations of the GPS unit used to survey horizontal sampling locations prior to the commencement of field work. The GPS training should include basic functions and capabilities of the unit, and the methods required to record location information to the level of accuracy required to meet the objectives of the Project.

2.5.2 Health and Safety Training

Health and safety procedures and training requirements are documented in the SSP (Anchor QEA 2019b). On-Site personnel will review and sign the SSP prior to the start of work.

All personnel who will participate in intrusive aspects of the field sampling program where contact with contaminated environmental media may occur must present to the Anchor QEA FSM a certificate of completion for an initial 40-hour hazardous waste operations and emergency response training course and the most recent certificate of completion for an 8-hour refresher course.

2.5.3 Laboratory Accreditation

Laboratories are required to hold DNR accreditation for analyses where accreditation is available. Currently, no accreditation is offered for PFAS analyses.

2.6 Documentation and Records

This section defines the records that are critical to the Project, identifies information to be included in the reports, and describes the data reporting format and document control procedures to be used. Project information generated by Anchor QEA will be documented in a format that is usable by all Project personnel. Specification of the proper reporting format, compatible with data validation, will facilitate clear and direct communication of the investigation. Project data and information will be tracked and managed from its inception in the field to its final storage area.

2.6.1 Document Control

Central Project files will be maintained by Anchor QEA. Project records will be stored and maintained in a secure manner. Each Project team member is responsible for filing necessary Project information

or providing it to the person responsible for the filing system. Individual team members may maintain files for individual tasks but must provide such files to the central Project files upon completion of each task. Hard copy documents will be kept on file for a minimum of 7 years by Anchor QEA or at a document storage facility throughout the duration of the Project, and electronic data will be maintained in Anchor QEA central database and server and backed up regularly as part of routine file maintenance.

2.6.2 Field Documentation

The field records to be used in this investigation will document field procedures and any measurements performed during the sampling effort. The Anchor QEA sampling team will maintain a field logbook (or tablet for electronic notes) to record sample collection and processing notes and to provide a daily record of significant events, observations, and measurements taken during the field investigation and any deviations from the FSP. All entries into the field logbook will be made with indelible ink. The field logbook (or tablet) is intended to provide sufficient data and observations to enable the field team to reconstruct events that occur during the Project.

The field logbook or tablet field notes will contain the following as a minimum:

- Sample collection team names
- Date and military time of collection
- Weather conditions, including temperature
- Site name and Project number
- Sample location
- Sample identification number
- Sample type
- Calculations, results, and calibration data for field sampling, field analytical, and field physical measurement equipment
- Any field measurements taken
- Field observations, especially any notice of stained sediment, stressed or absent vegetation, and presence of invasive species
- References such as maps or photographs of the sampling site
- Any procedural steps taken that deviate from those presented in this QAPP or the FSP (Anchor QEA 2019a)

Documents, records, photographs, and information relating to field activities will be maintained in the Project file via electronic files and/or hard copy. The Anchor QEA FTL will review field documentation to verify the activities met the intent of the FSP. Field logbooks or tablet, field sheets, and photographs will be scanned/uploaded daily (if possible) and stored electronically.

Other records of sample collection activities will include sample collection logs, chain-of-custody records, custody seals, sample labels, phone conversation records, airbills, and corrective action reports. Chain-of-custody records will be used to document the progression of field samples and QC samples and are discussed further in Section 3.3.

2.6.3 Laboratory Documentation

The analytical laboratories will be responsible for maintaining analytical logbooks and laboratory data. Raw laboratory data files and electronic and hard copy data will be inventoried and maintained by the laboratory for the time period established by EPA and the laboratory.

Laboratory analytical data packages will contain the following information at a minimum: case narrative, completed chain-of-custody forms, QC summary forms, blank results, sample result forms with MDLs and MRLs, calibration information, and raw data. The laboratories will provide an electronic copy of the data, which will be in the Anchor QEA custom EQuIS and Staged Electronic Data Deliverable (SEDD) formats.

2.6.4 Data Submittals

A data usability assessment will be included in the Site Investigation Report (SIR) and PFAS Special Study Report submitted by Anchor QEA to DNR. Analytical report narratives and data validation reports will be included with these reports.

Laboratory EDDs containing chemical data will be checked prior to submitting to Anchor QEA.

The SIR will provide the findings of the investigation within the SMC Investigation Area, including, but not limited to, data tables and maps summarizing the results and analysis.

The PFAS Special Study Report will provide the findings of the PFAS investigation within the MKE AOC, including, but not limited to, data tables and maps summarizing the results and analysis.

These deliverables will be submitted in both draft and final form, describing the sample number, location, results, data analysis, and recommendations (if any) from this assessment. The reports will also document sampling changes made in the field, along with any issues, concerns, or problems encountered during data collection and analysis. The draft report will be provided to the DNR Project Manager electronically on the date indicated in the Project schedule.

The Anchor QEA Project Manager will confirm that all Anchor QEA team members and subcontractors have the most current version of any planning documents or submittals. Prior to submitting any document to Anchor QEA, the subconsultant providing laboratory data will be responsible to Anchor QEA for the technical accuracy of the documents.

2.6.5 Project Data Assessment Records

Records of Project assessments will be maintained by the Anchor QEA Project Manager and Anchor QEA Project QC Manager, and may include field technical system audit checklists, field performance audit checklists, laboratory performance audit checklists, data validation reports, and internal reviewer sign-off.

3 Data Generation and Acquisition

Data generation and acquisition begins with the development of the rationale for locating and selecting environmental samples for analysis and ends with the generation and reporting of analytical data for those samples by the analytical laboratories.

3.1 Sampling Process Design

The sampling process design including the rationale for locating and selecting environmental samples for analyses is detailed in the FSP (Anchor QEA 2019a) and summarized in Table 6.

3.1.1 Sampling Approach, Methods, and Rationale

The overall sampling approach, methods, and rationale, as well as proposed sampling locations, are presented in the FSP (Anchor QEA 2019a).

3.1.2 Parameters to be Tested and Frequency

Sediment and water samples will be analyzed for the parameters specified in Tables 2 and 3. Sample locations and the associated analyses to be conducted are in Tables 4 through 5 of the FSP (Anchor QEA 2019a). Table 6 of the FSP provides the estimated number of samples (including field and laboratory QC samples) by program, matrix, and parameter.

3.2 Sampling Method Requirements

The use of proper sampling equipment, strict controls in the field, and appropriate chain-of-custody and analytical procedures will reduce the potential for sample misrepresentation and the collection of unreliable analytical data.

Sampling methods and equipment and decontamination protocols are presented in the FSP (Anchor QEA 2019a). As the probability of false positives is relatively high during PFAS sample collection due to the potential for many sources of cross-contamination, combined with low laboratory detection limits, additional decontamination protocols will be performed prior to PFAS sampling. PFAS are used in a wide variety of products; therefore, to prevent cross-contamination, field personnel should be familiar with and follow the MDEQ General PFAS Sampling Guidance (MDEQ 2018). Field forms and SOPs for sample collection, processing, and handling are provided in Appendix A of the FSP. Laboratory SOPs are provided in Attachment A of this QAPP, and sample handling, packaging, shipping, and chain-of-custody SOPs are provided in Appendix A of the FSP.

Samples will be preserved and shipped to CT, GEL, and ETA as outlined in FSP Appendix A SOP 07– Sample Handling, Packaging, and Shipping. The Anchor QEA Project QC Manager will be responsible for ensuring that sampling and analysis activities adhere to the requirements of this QAPP, the FSP, and attached SOPs.

3.3 Sample Handling and Custody Requirements

The primary objective of sample handling and custody procedures is to create an accurate written record that can be used to trace the possession and handling of samples from the moment of their collection, through analysis, until their final disposition. Procedures for sample labeling, handling, and reporting of Anchor QEA's environmental samples will comply with EPA-approved labeling and chain-of-custody protocols. Specific protocols for sample designation are presented in SOP 01 (Field Records) of the FSP, and specific protocols for sample handling, packaging, shipping, and custody are presented in SOP 06 (Sample Custody) and SOP 07 (Sample Handling, Packaging, and Shipping) in Appendix A of the FSP.

3.3.1 Sample Containers and Handling

Table 9 presents the required sample containers, sample preservation methods, and maximum holding times for the proposed analyses. Samples will be placed in appropriate sample containers and labeled. Certified, pre-cleaned sample containers will be obtained from the respective laboratories. These containers will meet and/or exceed EPA standards for pre-cleaned containers (EPA 1992). Samples will be packed and shipped in accordance with SOP 07 (Sample Handling, Packaging, and Shipping) in Appendix A of the FSP.

3.3.2 Documentation

Field efforts will be documented using field logbooks or tablets, field data forms, electronic-generated sample labels, sample chain-of-custody records, and custody seals. In addition, hard copies of this QAPP, the FSP, and the SSP will be kept on site for the duration of the field effort. General information will be recorded in the field logbook (or tablet) daily, including personnel present at the Site, sampling activities, and weather (see FSP Appendix A SOP 01 – Field Records). Sample collection and processing information will be recorded on the appropriate forms in FSP SOP 03 (Sediment Sampling), SOP 04 (Sediment Core Processing), and SOP 05 (Water Sampling). Collection and processing logs will include the following, as applicable to each log:

- Date and time of collection/processing
- Sample location identification
- Core penetration and recovery
- Material description
- Sample intervals collected
- Containers filled
- Water sample depth
- Personnel

Sample labels will include project identification, sample identification, date/time, analysis to be performed, preservation requirements, and sampler's initials. From the electronic database (or handwritten logbook), a chain-of-custody record will list all samples and requested analyses. Field logbooks and forms will be scanned daily (if possible) and saved electronically to the appropriate Anchor QEA internal Project folder.

3.3.3 Sample Custody – Overview

To maintain and document sample custody, chain-of-custody procedures will be strictly followed. A sample is considered to be under custody under the following conditions:

- It is in the custodian's possession or view
- It is in a secured location (under lock) with restricted access
- It is in a container that is secured with an official seal(s) such that the sample cannot be reached without breaking the seal(s)

By this definition, Anchor QEA field crew collecting the samples are responsible for care and custody of the sample until it is transferred to the shipping company.

3.3.4 Chain-of-Custody Records

Chain-of-custody records will be used to track all samples from the time of sampling to the arrival of samples at the laboratory and to final sample disposition. Each chain-of-custody form will be produced using an electronic database (or handwritten logbook). Every sample container being shipped, delivered, or picked up by the laboratory will contain a chain-of-custody record. Field personnel will retain a signed and dated hard copy and scanned electronic copy of the chain-of-custody, whereas the original chain-of-custody and other copies (if necessary) are enclosed in a waterproof enclosure within each shipping container. The laboratory, upon receiving the samples, will sign the original chain-of-custody and retain it in the Project file.

When transferring the possession of samples, the individuals relinquishing and receiving will sign, print their name, date, and note the time on the record. This record documents the transfer of samples from the custody of the sampler to that of another person, or the laboratory. Packaged samples will be accompanied by the chain-of-custody record, which identifies the contents. The sampler will retain a copy for the Project file.

The airbill number will be written on the chain-of-custody record retained by the field personnel. The Project Manager is responsible for consistency of records and inclusion in the permanent Project file.

3.3.5 Sampling and Packaging Procedures

Samples shipped to the laboratories will be packaged in compliance with current U.S. Department of Transportation regulations to avoid breakage or contamination. All sample caps will be tightened,

and the exterior of all sample bottles wiped down. In preparation for shipment to the laboratories, all samples will be packaged in accordance with the SOP 07 (Sample Handling, Packaging, and Shipping) in Appendix A of the FSP.

3.3.6 Sample Shipping Procedures

All samples will be shipped from the field to the appropriate laboratory for analysis. Table 10 provides the each of the laboratories, their address, and analysis type.

The following transfer of custody and shipment procedures will be followed:

- Samples will be accompanied by a completed, electronic-generated or handwritten chain-of-custody record. The sample IDs will be listed on the chain-of-custody record. When transferring the possession of samples, the individuals relinquishing (field team) and receiving (laboratory personnel) will sign and record the date and time on the record. This record documents transfer of custody of samples from the sampler to another person, to the laboratory, or to/from a secure storage area.
- Samples will be properly packaged for overnight shipment or same-day courier collection and dispatched to the laboratory for analysis, with a separate signed chain-of-custody record enclosed in each sample box or cooler. If the cooler is being shipped to the laboratory, it will be secured shut with clear packing tape over signed and dated custody seals to prevent tampering.
- All shipments will be accompanied by the chain-of-custody record identifying the contents.

3.3.7 Laboratory Chain-of-Custody Procedures

The laboratory chain-of-custody procedures and document control will be carried out according to the laboratory procedures detailed in each laboratory's QA manual and SOPs. The laboratory representative who accepts the incoming sample shipment will sign and date the chain-of-custody record to acknowledge receipt of the samples. Once the sample transfer process is complete, the laboratory is responsible for maintaining internal logbooks and records that provide a custody record throughout sample preparation and analysis.

If more than one laboratory handles the samples, custody of the samples is maintained between laboratory sample management personnel. Within each laboratory, the analysts will maintain custody of the sample while the analysis is being performed.

3.4 Analytical Methods Requirements

Analyses will be performed following the methods identified in Tables 2 and 3. Detailed descriptions of the analytical procedures, including instrument method performance criteria and corrective actions, can be found in the laboratory SOPs (Attachment A).

3.5 Quality Control Requirements

QC is defined as 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 established requirements. Field and laboratory QC samples are collected during the field investigation and created in the laboratory to evaluate field and laboratory variability.

This section of the QAPP identifies the QC procedures, checks, and samples that will be used during the Project to monitor the quality of various aspects of the sampling events and laboratory methodology. Required analysis frequency, acceptance limits, and corrective actions are documented in this section of the QAPP.

3.5.1 Field Quality Control Checks

Field QC checks are used to assess the reliability, repeatability, and statistical confidence of the data that are collected. They are designed to determine what effects activities such as sample collection, bottling, shipping, and storage have on sample integrity, and that samples available for analysis in the laboratory are representative of actual conditions on the Site. Field QC checks, which will be conducted in accordance with the applicable procedures (SOPs) and frequencies described in this QAPP and the FSP (Anchor QEA 2019a), include the following:

- **Rinsate blank**—One equipment rinsate blank per sample matrix and collection method will be collected per 20 samples to assess and document the adequacy of the decontamination process. A rinsate blank is a sample of analyte-free water poured over or through decontaminated sampling equipment prior to collection of field samples. Rinsate blanks will be analyzed for metals, PCBs, PAHs, and PFAS.
- **Field blank**—One field blank associated with PFAS water sample collection will be collected following clean sampling techniques as described in the MDEQ General PFAS Sampling Guidance (MDEQ 2018) and EPA Method 1669, as applicable to PFAS sample collection. The field blank consists of pouring PFAS-free water into appropriate sample containers.
- **Field duplicate**—A field duplicate is a second sample taken from the homogenized material that comprises the original sample. The purpose of a field duplicate sample is to evaluate the effectiveness of homogenization techniques and material heterogeneity for the Site material and the variability of a given analysis. One field duplicate will be collected for every set (or partial set) of 20 samples collected per media. The precision goal for field duplicates for this Project is ±50% RPD.
- **Field audit**—An audit of field activities (see Field Audit Checklist provided in Attachment B of this QAPP) to ensure work is being conducted as described in the FSP (Anchor QEA 2019a) will be completed at least once during the field investigation.

3.5.2 Laboratory Quality Control Checks

Internal laboratory QC procedures for the sample analyses are specified in the analytical methods and respective laboratory SOPs. These specifications include the types of QC checks required (method blanks, instrument blanks, LCSs, MS/MSDs, calibration standards, internal standards, surrogate standards, specific calibration check standards, laboratory duplicate/replicate analysis), compounds and concentrations to be used, and the QC acceptance criteria for these QC checks. The project QC acceptance criteria are in Table 7. Additional mass for matrix duplicate (MD)/MS/MSD analyses will be collected at a frequency of 5% of total samples. Details regarding the laboratory control limits and procedures for calculation of the appropriate QC statistics can be found in the laboratory analytical SOPs (Attachment A).

3.6 Instrument/Equipment Preventive Maintenance

This section describes procedures for testing, inspection, and maintenance of field and laboratory equipment.

3.6.1 Field Instruments/Equipment and Calibration

In accordance with the QA program, Anchor QEA and its subconsultants' shall maintain an inventory of field instruments and equipment. The frequency and types of maintenance will be based on the manufacturer's recommendations and previous experience with the equipment.

The Anchor QEA FTL will be responsible for the preparation, documentation, and implementation of the preventive maintenance program. The equipment maintenance information will be documented on the instrument's calibration log. The frequency of maintenance is dependent on the type and stability of the equipment, the methods used, the intended use of the equipment, and the recommendations of the manufacturer. Detailed information regarding the calibration and frequency of equipment calibration is provided in the manufacturer's instruction manuals.

All maintenance records will be verified prior to each sampling event. The Anchor QEA FTL will be responsible for verifying that required maintenance has been performed prior to using the equipment in the field. For this Project, maintenance inspections will include the following activities:

- The subcontractor responsible for navigation will confirm proper operation of the navigation equipment daily. This verification may consist of internal diagnostics or visiting a location with known coordinates to confirm the coordinates indicated by the navigation system.
- The winch line, as well as sediment samplers, will be inspected daily for fraying, misalignment, loose connections, and any other applicable mechanical problems.
- The water quality sonde calibration will be checked daily to ensure it is operating within manufacturer's specifications.

Any problems will be noted in the field logbook and corrected prior to continuing sampling operations.

3.6.2 Laboratory Instruments

In accordance with the QA program, the laboratory shall maintain an inventory of instruments and equipment, and the frequency of maintenance will be based on the manufacturer's recommendations and/or previous experience with the equipment.

The laboratory preventative maintenance program, as detailed in the laboratory QA Plan, is organized to maintain proper instrument and equipment performance and to prevent instrument and equipment failure during use. The program considers instrumentation, equipment, and parts that are subject to wear, deterioration, or other changes in operational characteristics, the availability of spare parts, and the frequency at which maintenance is required. Any equipment that has been overloaded, mishandled, gives suspect results, or has been determined to be defective will be taken out of service, tagged with the discrepancy noted, and stored in a designated area until the equipment has been repaired. After repair, the equipment will be tested to ensure that it is in proper operational condition. The client will be promptly notified in writing if defective equipment casts doubt on the validity of analytical data. The client will also be notified immediately regarding any delays due to instrument malfunctions that could impact holding or turnaround times.

Laboratories will be responsible for the preparation, documentation, and implementation of the preventative maintenance program. Maintenance records will be checked according to the schedule on an annual basis and recorded by laboratory personnel. The Laboratory QA/QC Manager or designee shall be responsible for verifying compliance.

3.6.2.1 Laboratory Instrument/Equipment Calibration

As part of their QC program, laboratories perform two types of calibrations. A periodic calibration is performed at prescribed intervals (e.g., balances, drying ovens, refrigerators, and thermometers), and operational calibrations are performed daily, at a specified frequency, or prior to analysis (i.e., initial calibrations) according to method requirement. Calibration protocols and frequency requirements are described in the laboratory analytical SOPs (Attachment A).

The Laboratory QA/QC Manager will be responsible for ensuring that the laboratory instrumentation is calibrated in accordance to specifications. Implementation of the calibration program will be the responsibility of the respective laboratory group supervisors. Recognized procedures (EPA, ASTM, Standard Method, or manufacturer's instructions) will be used when available.

Physical standards (i.e., weights or certified thermometers) will be traceable to nationally recognized standards such as the National Institute of Standards and Technology (NIST). Chemical reference

standards will be NIST standard reference materials or vendor-certified materials traceable to these standards.

The calibration requirements for each method and respective corrective actions will be accessible, either in the laboratory SOPs or in the laboratory's QA Plan for each instrument or analytical method in use. All calibrations will be preserved on electronic media.

3.7 Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and consumables that may directly or indirectly affect the quality of the Project must be clearly identified and documented by field personnel. Typical examples of supplies and consumables include sample bottles, sample collection and processing equipment, and materials for decontamination activities.

Acceptance criteria must be consistent with overall Project technical and quality criteria. If there are special requirements for particular supplies or consumables, a clear agreement should be established with the supplier (e.g., particular concentration of calibration gas).

Only pre-cleaned, certified sample containers and lids will be used for the proposed analyses. The pre-cleaned sample containers will be provided by the laboratories with individual certification. Prior to use, Anchor QEA and its subconsultants' field staff will inspect sample containers and other Project materials to verify their cleanliness and usability. Any observed deficiencies that may affect the quality of the sample data should be documented and reported to the Anchor QEA Project Manager. Anchor QEA will also provide appropriate supplies for homogenizing samples prior to filling the sample container, as required and described in SOP 04 (Sediment Core Processing) in Appendix A of the FSP (Anchor QEA 2019a).

3.8 Data Acquisition Requirements for Non-Direct Measurements

For this Project, Anchor QEA and its subconsultants' may acquire data from non-direct measurements (e.g., field observations during sample collection). In these instances, photographic documentation or field data sheets may be used to record the data.

Field observations are standard practice for many types of investigations. These data are used in a weight-of-evidence approach to substantiate direct measurement data. However, these data are generally not used as the only source for a decision point.

3.9 Data Management

Data management is a process for tracking data from generation in the field and/or laboratory to final use and storage. Once the data have been provided to Anchor QEA by the analytical laboratory, the data will be retrieved, recorded, reduced, assessed, tracked, and stored in the Project-specific

network folders, which are backed up at least once per day to a recordable media. Technical data, including field observations, laboratory analytical results, and validated analytical data, will be stored in EQuIS. The EQuIS database resides on individual Anchor QEA computers/tablets, and the Microsoft SQL network server that is backed up daily. To certify data are accurately recorded and stored, tracking systems will be implemented. The Anchor QEA Project QC Manager, Data Manager, and/or designee will conduct automated and manual QC checks to verify that data have been accurately recorded and appropriately stored. Corrective actions will be taken in the event that data have not been properly handled. The progress of sample collection and processing will be monitored through the documentation of samples collected, processed, and shipped each day.

3.9.1 Field Measurements and Sample Collection

The field operating records to be used in this investigation will document field procedures and any measurements performed during the sampling effort. A discussion of field operation records is presented in Section 2.6.2 of this QAPP. The Anchor QEA FTL will compile the field data and provide it to the Anchor QEA Project QC Manager to review, reduce, and upload into the EQuIS database. Field data transferred from written records to the field data EDDs will be reviewed for accuracy and completeness before loading into the database. Field data that cannot be integrated into the database (e.g., photographs or logbooks) will be stored electronically in the Project-specific network folders and/or in the paper Project folders, along with supporting metadata such as author/creator of data, date, location, and a brief description. The Anchor QEA FTL and Anchor QEA Project QC Manager will be responsible for the storage of field data files, either stored electronically in the Project-specific network folders or in the paper Project folders.

3.9.2 Laboratory Reporting and Recordkeeping

The laboratories will prepare and submit data packages of the analytical and associated QA/QC results. Analytical data will be transmitted from the laboratories in PDF and EDD formats. Analytical laboratory reports submitted will be stored electronically in the Project-specific network folders. Analytical data results received from the laboratory will be checked for completeness by comparing them to the chain-of-custody documentation and the workplans.

Each laboratory data package will include the following (as applicable):

- A cover letter
- Case narrative, including statement of samples received, description of any deviations from standard procedures, explanation of qualifications regarding data quality, and any other significant problems encountered during analysis
- A summary of sample results that will include the following information when applicable:
  - Field sample identification code and the corresponding laboratory identification code
  - Sample matrix

  - Date of sample preparation/extraction
  - Preparation and analytical batch identifications
  - Date and time of analysis
  - Mass or volume used for preparation and analysis
  - Final dilution or concentration factors for the sample
  - Identification of the instrument used for analysis
  - MDLs and MRLs accounting for sample-specific factors (e.g., dilution and total solids)
  - Analytical results with reporting units identified
  - Data qualifiers and their definitions
- QA/QC summaries, including, but not limited to, the following:
  - Method blank results
  - Surrogate spike recoveries
  - Internal standard area counts
  - Second column confirmation RPD values
  - MS/MSD recoveries and RPD values
  - Matrix duplicate RPD values
  - LCS recoveries
  - Interference check samples
  - Serial dilutions
- Calibration data summary
- Original data, including
  - Sample extraction, preparation, and cleanup logs
  - Instrument run logs
  - Instrument tunes
  - Ion chromatograms
  - Enhanced spectra of detected compounds with reference spectra
  - Quantitation reports
- Field and laboratory chain-of-custody documentation pertaining to each sample delivery group analyzed

The Laboratory Project Manager or appropriate personnel assigned by the Laboratory Project Manager, as part of the data validation process, will confirm the following: documentation is complete and legible; qualitative identifications are accurate; calculations are accurate; results are expressed in the appropriate units and number of significant figures; and the required QC checks were run and met acceptance criteria. All pages in analytical data packages will be consecutively numbered. Review and approval of the data will be documented by the Laboratory Project Manager.

4 Assessment and Oversight

This section details the procedures used for implementation of this QAPP.

4.1 Assessment and Response Actions

After data are received from the laboratory, a number of QC procedures will be followed to evaluate data quality. Specific procedures will also be followed to assess data precision, accuracy, and completeness.

4.2 Compliance Assessments

Performance audits consist of on-Site reviews of QA systems and equipment for sampling, calibration, and measurement. Laboratory performance audits will not be conducted as part of this study; however, laboratory audit reports will be made available to the Project QC Manager upon request. The laboratory is required to have written procedures addressing internal QA/QC. The laboratory must ensure that personnel engaged in preparation and analysis tasks have appropriate training. As part of the audit process, the laboratory will provide written details of any method modifications planned for the consultant's review.

4.3 Response and Corrective Actions

The following sections identify the responsibilities of key Project team members and actions to be taken in the event of an error, problem, or non-conformance of protocols identified in this document.

4.3.1 Field Activities

The Anchor QEA FTL will be responsible for correcting equipment malfunctions during the field sampling effort. The Anchor QEA Project QC Manager will be responsible for resolving situations identified by Anchor QEA FTL that may result in non-compliance with this QAPP. Corrective measures will be immediately documented in the field logbook and reported to the DNR Project Manager and EPA Sediment Task Force Lead.

4.3.2 Laboratories

The laboratories are required to comply with their SOPs (Attachment A). The Laboratory Managers will be responsible for ensuring that appropriate corrective actions are initiated as required for conformance with this QAPP. Laboratory personnel will be responsible for reporting problems that may compromise the quality of the data.

4.4 Reports to Management

QA reports to management include verbal status reports, data validation reports, and final laboratory reports. These reports shall be the responsibility of the Anchor QEA Project QC Manager. Verbal status reports include updates from the Anchor QEA Project QC Manager to the Anchor QEA Project Manager or designee on laboratory reporting progress, data validation progress, and any issues resulting in data rejection. Updates will be given as needed in routinely scheduled Project meetings.

The field activities performed and field data will be documented as described in the FSP. The laboratory-based activities performed and sample results will be documented as described in the attached SOPs.

Anchor QEA Project Manager will be responsible for preparation of all reporting.

5 Data Validation and Usability

The purpose of this section is to state the criteria for deciding the degree to which each dataset has met its quality specifications. Validation and verification procedures that will be conducted during sample collection and data generation are presented below. Conformance to these procedures will certify the representativeness of the samples and that sample integrity is maintained from sample collection through analysis at the laboratory. Data generated by the laboratories will be submitted to Anchor QEA and assessed for completeness. Anchor QEA will track the analytical data packages and EDDs through the data validation process. The data will be reviewed by the Anchor QEA Project QC Manager following validation to determine its usability for decision-making and reporting activities. A data usability assessment, prepared by the Anchor QEA Project QC Manager, will be included within the SIR and PFAS Special Study Report.

The following two steps are required to document that Project data quality standards are met:

1. **Data verification and validation**—Data verification and validation consist of evaluating the completeness, correctness, and conformance or contractual compliance of a dataset against the method standard, SOP, or contract requirements documented in the Project QAPP.
2. **Data usability assessment**—Data usability assessment is the process of evaluating verified and validated data to determine whether they can be used for the purpose of the Project.

5.1 Review, Validation, and Verification Requirements

Data generated during field and laboratory activities will be reduced, reviewed, and validated prior to reporting.

5.1.1 Data Reduction and Review

Raw data from any field measurements and sample collection activities will be appropriately recorded in the field logbook or tablet.

Laboratory data reduction procedures will be in accordance with each individual laboratory SOP (Attachment A). Laboratory methods to be followed in this investigation are listed in Tables 2 and 3. For each of the methods, the Laboratory Project Manager will complete a thorough inspection of all reports prior to release of the data. Following review and approval of the preliminary report by the Laboratory Project Manager, final reports will be generated and signed by the Laboratory Project Manager.

5.1.2 Data Validation

During the validation process, field and analytical data will be evaluated for Project, method, and laboratory QC compliance, as applicable, and their validity and applicability for program purposes will be determined. Based on the findings of the validation process, data validation qualifiers may be

assigned. The validated Project data, including qualifiers, will be entered into the Project database, thus enabling this information to be retained or retrieved, as needed.

Completeness will be evaluated by auditing the data package for the following:

- Chain-of-custody records
- Technical holding times
- Required analytical methods and analyte lists
- MDLs and MRLs
- Reporting format
- Laboratory and field QC reporting forms (e.g., blanks, surrogates, duplicates, MS, as appropriate)
- Appropriate supporting data
- Case narrative
- Completeness of results
- Data usability

5.2 Validation and Verification Methods

An EPA Stage 2A (EPA 2009) data validation will be performed on all data and Stage 2B validations will be performed on 20% of the data. Validations will be completed by LDC and reviewed by the Anchor QEA Project QC Manager or designee. Validation for data usability will be accomplished by comparing the contents of the analytical data packages and QA/QC results to the requirements contained in this QAPP, the respective methods, and the laboratory SOPs (Attachment A).

General guidelines for data validation are presented in the following:

- *National Functional Guidelines for Organic Superfund Methods Data Review* (EPA 2017a)
- *National Functional Guidelines for Inorganic Superfund Methods Data Review* (EPA 2017b)

Data that are not covered in the functional guidelines will be compared against the applicable analytical methods, the laboratory SOPs, and guidelines described in this QAPP. The validator will apply qualifier flags to individual results based on their findings, using their best professional judgment, and consistent with the EPA National Functional Guidelines qualifier definitions.

Anchor QEA will review pertinent sampling and laboratory documentation to determine to what degree data have met their quality specifications as presented in this QAPP.

In coordination with the Anchor QEA FTL, data verification by the Anchor QEA Project QC Manager will include the following:

- **Sampling design**—Check each sample for conformity to the specifications, including type and location.

- **Sample collection procedures**—Verify that sample collection procedures were performed in accordance with procedures presented in the FSP and this QAPP. Any deviations shall be documented in the field logbook.
- **Sample handling**—Verify that the sample was labeled, documented, and shipped properly in accordance with procedures presented in the FSP and this QAPP.
- **Analytical procedures**—Verify that each sample was analyzed by the methods specified in this QAPP, as required.
- **Quality control**—Verify that QC was performed at the required frequency during sample collection, handling, and analyses.
- **Calibration**—Verify that the calibration of field instruments was performed in accordance with the manufacturer specifications for the equipment.

In the event that concerns are identified during data collection, review, verification, or validation processes, the Anchor QEA Project QC Manager will work with the DNR Project Manager, EPA Sediment Task Force Lead, and, if needed, analytical laboratories to develop an appropriate resolution.

Findings or QC concerns will be included in the Data Usability Report prepared by Anchor QEA. The Anchor QEA Project Manager, after consultation with the Anchor QEA Project QC Manager, will be responsible for any corrective action identified during the data validation process.

Initiation of laboratory corrective actions will be the responsibility of Anchor QEA Project Manager and/or Anchor QEA Project QC Manager.

5.3 Usability/Reconciliation with Data Quality Objectives

Laboratory results will be assessed for compliance with required precision, accuracy, completeness, and sensitivity requirements as described in Section 2.4 and Tables 7, 8, and 9 of this QAPP. Data that do not meet the specified requirements and the QA requirements in the analytical methods will be discussed in the data validation summaries and incorporated into the summary report for this Project.

The SIR and PFAS Special Study Report will summarize the findings from the field study, including but not limited to, data tables and maps summarizing the findings of the investigation. Qualifiers assigned by the validator will be applied to the database and included in all database exports, including tables in the reports.

Any sources of sampling or analytical error will be identified as early as possible during the ample collection activities so that corrective action can be quickly implemented. Data that are not deemed usable to support or address the Project decision-making process will be identified and the potential need for additional sampling will be discussed with the Anchor QEA Project Manager, DNR Project

Manager, and EPA Sediment Task Force Lead. A disclaimer will be included on each page of any table generated from the data and included in a report if the use of the data obtained from any sampling event should be limited for any reason. Data qualified as estimated during validation will be considered usable for the DQOs of this Project. No PCB results will be determined as unusable should extraction and/or analyses be conducted past specified hold times.

6 References

Anchor QEA (Anchor QEA, LLC), 2019a. *Field Sampling Plan.* Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS, Milwaukee, Wisconsin. November 2019.

Anchor QEA, 2019b. *Site Safety Plan*. Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS, Milwaukee, Wisconsin. November 2019.

CH2M, 2019. *Focused Feasibility Study Report – Menomonee and Milwaukee Rivers Milwaukee Estuary Area of Concern*. Milwaukee, Wisconsin. Task Order No. 0029. Contract No. EP-R5-11-09.

DNR (Wisconsin Department of Natural Resources), 1991. *Milwaukee Estuary Stage 1 Remedial Action Plan*. Contract No. PUBL-WR-276-91.

DNR 2017. *Draft Remedial Action Plan Update for the Milwaukee Estuary Area of Concern*. December 2017.

DNR 2019. *Professional Services Scope of Work for Characterization of sediments in the South Menomonee Canal and Milwaukee AOC PFAS Sampling*. September 2019.

EPA (U.S. Environmental Protection Agency), 1992. *Specifications and Guidance for Obtaining Contaminant-Free Sample Containers*. Office of Solid Waste and Emergency Response Directive No. 9240.0-05A. April 1992.

EPA, 2001. *EPA Requirements for Quality Assurance Project Plans.* EPA QA/R-5. Office of Environmental Information. Washington, D.C. EPA/240/B-01/003. March 2001.

EPA, 2002. *EPA Guidance for Quality Assurance Project Plans.* EPA QA/G-5. Office of Environmental Information. Washington, D.C. EPA/240/R-02/009. December 2002.

EPA, 2006. *Guidance on Systematic Planning Using the Data Quality Objectives Process.* EPA QA/G-4. Office of Environmental Information. Washington, D.C. EPA/240/B-06/001. February 2006.

EPA, 2009. *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use*. Office of Solid Waste and Emergency Response No. 9200.1-85, EPA 540-R-08-005. January 2009.

EPA, 2017a. *National Functional Guidelines for Organic Superfund Methods Data Review*. Office of Superfund Remediation and Technology Innovation (OSRTI). EPA-540-R-2017-002. January 2017.

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EPA, 2019. *SEDD Specification and Data Element Dictionary, Version 5.2, for the Staged Electronic Data Deliverable (SEDD)*. EPA-542-B-19-001. Available at: https://www.epa.gov/sites/production/files/2019-05/documents/sedd_spec_v5-2-march_2019_508.pdf. March 2019.

MDEQ (Michigan Department of Environmental Quality), 2018. *Michigan Department of Environmental Quality General PFAS Sampling Guidance*. Revised October 16, 2018.

Tables

Table 1

Project Distribution and Contact List

QAPP Recipient	Title	Organization	Telephone Number	Email Address
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Christina Rink	Data Validator	Laboratory Data Consultants	760.827.1100 ext. 161	crink@lab-data.com

Notes:
DNR: Department of Natural Resources
EPA: U.S. Environmental Protection Agency
GLNPO: Great Lakes National Program Office
QA: Quality Assurance
QAPP: Quality Assurance Project Plan

Table 2

Sediment Analytes, Methods, and Target Reporting Limits

Parameter	Analytical Method	PEC[1]	Laboratory MDLs	Laboratory MRLs
Conventionals (%)				
Total solids	SM 2540G	--	0.1	0.1
Total organic carbon (TOC)	9060A	--	0.0036	0.03
Geotechnical				
Grain size (%)	ASTM D422-63	--	--	0.1
Atterberg limits	ASTM D4318-05	--	--	--
Specific gravity	ASTM D854-06	--	--	--
Moisture content	ASTM D2216-05	--	--	--
Metals (mg/kg)				
Arsenic	6010C	33	0.13	0.80
Cadmium	6010C	4.98	0.006	0.040
Chromium	6010C	111	0.023	0.14
Copper	6010C	149	0.07	0.40
Lead	6010C	128	0.04	0.25
Mercury	7471A	1.06	0.0021	0.0083
Nickel	6010C	48.6	0.021	0.120
Zinc	6010C	459	0.05	0.30
Polycyclic Aromatic Hydrocarbons (µg/kg)				
2-Methylnaphthalene	8270D - SIM	--	0.31	2.00
Acenaphthene	8270D - SIM	--	0.29	2.00
Acenaphthylene	8270D - SIM	--	0.26	2.00
Anthracene	8270D - SIM	845	0.4	2.0
Benzo(a)anthracene	8270D - SIM	1050	0.5	2.0
Benzo(a)pyrene	8270D - SIM	1450	0.4	2.0
Benzo(b)fluoranthene	8270D - SIM	--	0.5	2.0
Benzo(e)pyrene	8270D - SIM	--	0.7	2.3
Benzo(g,h,i)perylene	8270D - SIM	--	0.6	2.0
Benzo(k)fluoranthene	8270D - SIM	--	0.9	2.8
Chrysene	8270D - SIM	1290	0.6	2.0
Dibenzo(a,h)anthracene	8270D - SIM	--	0.6	2.1
Fluoranthene	8270D - SIM	--	0.4	2.0
Fluorene	8270D - SIM	536	0.27	2.00
Indeno(1,2,3-cd)pyrene	8270D - SIM	--	0.5	2.0
Naphthalene	8270D - SIM	561	0.3	2.0
Phenanthrene	8270D - SIM	1170	0.3	2.0
Pyrene	8270D - SIM	1520	0.4	2.0
Polychlorinated Biphenyl Aroclors (µg/kg)				
Aroclor 1016	8082A	--	18	30
Aroclor 1221	8082A	--	25	30
Aroclor 1232	8082A	--	30	30
Aroclor 1242	8082A	--	23	30
Aroclor 1248	8082A	--	22	30
Aroclor 1254	8082A	--	30	30
Aroclor 1260	8082A	--	18	30
Aroclor 1262	8082A	--	25	30
Aroclor 1268	8082A	--	18	30
Total PCBs	--	676	--	--

Table 2
Sediment Analytes, Methods, and Target Reporting Limits

Notes:
µg/kg: micrograms per kilogram
MDL: method detection limit
mg/kg: milligrams per kilogram
MRL: method reporting limit
PEC: Probable Effects Concentration

1 Ingersoll, et. al, 2000 (https://www.cerc.usgs.gov/pubs/center/pdfdocs/91126.pdf)

2 Results will be screened against the PED, 2xPEC, and 3xPEC for metals and PAHS. Total PCBs will be screened against 1 mg/kg, 10 mg/kg, and 50 mg/kg.

Table 3
PFAS and Related Analyses

Parameter	Analytical Method	MDL	MRL
Sediment			
Conventionals (%)			
Total solids	SM 2540G	0.1	0.1
Total organic carbon (TOC)	9060A	0.02	0.05
Geotechnical			
Grain size (%)	ASTM D422-63	--	0.1
Atterberg limits	ASTM D4318-05	--	--
Specific gravity	ASTM D854-06	--	--
Moisture content	ASTM D2216-05	--	--
Perfluoroalkyl and Polyfluoroalkyl Substances (µg/kg)[1]			
Perfluorobutyric acid (PFBA)	GL-OA-E-076[2]	0.165	0.5
Perfluoropentanoic acid (PFPeA)	GL-OA-E-076[2]	0.165	0.5
Perfluorohexanoic acid (PFHxA)	GL-OA-E-076[2]	0.165	0.5
Perfluoroheptanoic acid (PFHpA)	GL-OA-E-076[2]	0.165	0.5
Perfluorooctanoic acid (PFOA)	GL-OA-E-076[2]	0.165	0.5
Perfluorononanoic acid (PFNA)	GL-OA-E-076[2]	0.165	0.5
Perfluorodecanoic acid (PFDA)	GL-OA-E-076[2]	0.37	1
Perfluoroundecanoic acid (PFUdA)	GL-OA-E-076[2]	0.165	0.5
Perfluorododecanoic acid (PFDoA)	GL-OA-E-076[2]	0.165	0.5
Perfluorotridecanoic acid (PFTrDA)	GL-OA-E-076[2]	0.165	0.5
Perfluorotetradecanoic acid (PFTeDA)	GL-OA-E-076[2]	0.165	0.5
Perfluorohexadecanoic acid (PFHxDA)	GL-OA-E-076[2]	0.165	1
Perfluorooctadecanoic acid (PFODA)	GL-OA-E-076[2]	0.39	1
Perfluorobutanesulfonate (PFBS)	GL-OA-E-076[2]	0.165	0.5
Perfluoropentanesulfonate (PFPeS)	GL-OA-E-076[2]	0.165	0.5
Perfluorohexanesulfonate (PFHxS)	GL-OA-E-076[2]	0.165	0.5
Perfluoroheptanesulfonate (PFHpS)	GL-OA-E-076[2]	0.185	0.5
Perfluorooctanesulfonate (PFOS)	GL-OA-E-076[2]	0.165	0.5
Perfluorononanesulfonate (PFNS)	GL-OA-E-076[2]	0.165	0.5
Perfluorodecanesulfonate (PFDS)	GL-OA-E-076[2]	0.165	0.5
Perfluoro-1-dodecanesulfonate (PFDoS)	GL-OA-E-076[2]	TBD	TBD
Fluorotelomer sulfonate 4:2 (4:2 FTS)	GL-OA-E-076[2]	0.4	1
Fluorotelomer sulfonate 6:2 (6:2 FTS)	GL-OA-E-076[2]	0.39	1
Fluorotelomer sulfonate 8:2 (8:2 FTS)	GL-OA-E-076[2]	0.385	1
Fluorotelomer sulfonate 10:2 (10:2 FTS)	GL-OA-E-076[2]	0.33	1
Perfluorooctanesulfonamide (PFOSA)	GL-OA-E-076[2]	0.165	0.5
N-methylperfluoro-1-octanesulfonamide (N-MeFOSA)	GL-OA-E-076[2]	0.435	1
N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)	GL-OA-E-076[2]	0.41	1
N-methylperfluoro-1-octanesulfonamidoacetic acid	GL-OA-E-076[2]	0.33	1
N-ethylperfluoro-1-octanesulfonamidoacetic acid	GL-OA-E-076[2]	0.275	1
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	GL-OA-E-076[2]	0.39	1
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	GL-OA-E-076[2]	0.395	1
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (PFPrOPrA)	GL-OA-E-076[2]	0.165	0.5
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	GL-OA-E-076[2]	0.33	1
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (PF3ONS)	GL-OA-E-076[2]	0.33	1
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS)	GL-OA-E-076[2]	0.33	1
Water			
Conventionals (mg/L)			
Total suspended solids	SM 2540D	1.14	5.0

Table 3
PFAS and Related Analyses

Parameter	Analytical Method	MDL	MRL
Perfluoroalkyl and Polyfluoroalkyl Substances (µg/L)[1]			
Perfluorobutyric acid (PFBA)	GL-OA-E-076[2]	0.00066	0.002
Perfluoropentanoic acid (PFPeA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorohexanoic acid (PFHxA)	GL-OA-E-076[2]	0.00066	0.002
Perfluoroheptanoic acid (PFHpA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorooctanoic acid (PFOA)	GL-OA-E-076[2]	0.0007	0.002
Perfluorononanoic acid (PFNA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorodecanoic acid (PFDA)	GL-OA-E-076[2]	0.00078	0.002
Perfluoroundecanoic acid (PFUdA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorododecanoic acid (PFDoA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorotridecanoic acid (PFTrDA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorotetradecanoic acid (PFTeDA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorohexadecanoic acid (PFHxDA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorooctadecanoic acid (PFODA)	GL-OA-E-076[2]	0.00066	0.002
Perfluorobutanesulfonate (PFBS)	GL-OA-E-076[2]	0.00066	0.00178
Perfluoropentanesulfonate (PFPeS)	GL-OA-E-076[2]	0.00066	0.00188
Perfluorohexanesulfonate (PFHxS)	GL-OA-E-076[2]	0.00066	0.00182
Perfluoroheptanesulfonate (PFHpS)	GL-OA-E-076[2]	0.00066	0.0019
Perfluorooctanesulfonate (PFOS)	GL-OA-E-076[2]	0.0008	0.002
Perfluorononanesulfonate (PFNS)	GL-OA-E-076[2]	0.0007	0.00192
Perfluorodecanesulfonate (PFDS)	GL-OA-E-076[2]	0.00066	0.00194
Perfluoro-1-dodecanesulfonate (PFDoS)	GL-OA-E-076[2]	TBD	TBD
Fluorotelomer sulfonate 4:2 (4:2 FTS)	GL-OA-E-076[2]	0.00132	0.00376
Fluorotelomer sulfonate 6:2 (6:2 FTS)	GL-OA-E-076[2]	0.00132	0.0038
Fluorotelomer sulfonate 8:2 (8:2 FTS)	GL-OA-E-076[2]	0.00132	0.00384
Fluorotelomer sulfonate 10:2 (10:2 FTS)	GL-OA-E-076[2]	0.00132	0.00384
Perfluorooctanesulfonamide (PFOSA)	GL-OA-E-076[2]	0.00066	0.00186
N-methylperfluoro-1-octanesulfonamide (N-MeFOSA)	GL-OA-E-076[2]	0.00132	0.004
N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)	GL-OA-E-076[2]	0.00066	0.004
N-methylperfluoro-1-octanesulfonamidoacetic acid	GL-OA-E-076[2]	0.00132	0.004
N-ethylperfluoro-1-octanesulfonamidoacetic acid	GL-OA-E-076[2]	0.00132	0.004
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	GL-OA-E-076[2]	0.00066	0.002
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	GL-OA-E-076[2]	0.00066	0.002
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (PFPrOPrA)	GL-OA-E-076[2]	0.00066	0.002
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	GL-OA-E-076[2]	0.00066	0.002
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (PF3ONS)	GL-OA-E-076[2]	0.00066	0.00186
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS)	GL-OA-E-076[2]	0.00132	0.00377

Notes:
µg/kg: micrograms per kilogram
µg/L: micrograms per liter
MDL: method detection limit
mg/L: milligrams per liter
MRL: method reporting limit
PFAS: perfluoroalkyl and polyfluoroalkyl substances
TBD: to be determined. MDL studies in process and will be updated once complete.
1 At the time of this document submittal, no screening levels have been established for these compounds. Results for these will be evaluated in close coordination with WI DNR and GLNPO.
2 GEL SOP GL-OA-E-076, Rev. 7, May 2019. Will also follow WI DNR performance-based guidance (https://dnr.wi.gov/news/input/documents/guidance/draft/EA-19-0001-D.pdf)

Table 6
Data Quality Objectives

DQO Component						
Step 1: State the Problem	**Step 2: Identify the Goal of the Study**	**Step 3: Identify the Information Inputs**	**Step 4: Define the Boundaries of the Study**	**Step 5: Develop the Analytical Approach**	**Step 6: Specify Performance or Acceptance Criteria**	**Step 7: Develop the Plan for Obtaining Data**
Previous sampling within the Milwaukee River Estuary Area of Concern (MKE AOC) has shown elevated levels of metals, PCBs, and PAHs in sediments of the South Menomonee Canal (SMC). Furthermore, sampling conducted by the USACE homogenized sediment over the entire core length to understand composition of dredged material. Finer resolution sampling within the SMC is needed to understand depths of contamination for future remedial decision-making. To date, neither sediment nor surface water samples from the MKE AOC have been analyzed for PFAS.	Additional site characterization data are needed to properly assess the chemical and physical properties of the SMC to identify future areas of focus for further investigation or remediation. A PFAS Special Study is also needed to understand the presence of PFAS within the MKE AOC. Data obtained through this study will be used to assess future management option for the MKE AOC sediments.	**DQO 1:** Determine the horizontal extent of contaminated sediment (metals, PAHs, and PCBs) in the SMC.	The MKE AOC boundary as depicted in Figure 1 of the FSP. Sampling will be focused in the SMC as shown in Figure 2 of the FSP.	Sediment cores will be collected from 35 locations within the SMC, including 22 locations to characterize the SMC between the Menomonee River and Interstate 94, 11 locations to characterize the SMC from Interstate 94 to the canal termination, and 2 locations to characterize Burnham Canal downstream of the currently inoperative Canadian Pacific Railway Burnham swing bridge (Figure 2 of the FSP). Proposed locations were placed in a triangular grid pattern throughout the SMC and Burnham Canal to target both the navigation channel centerline and the side slope or area between the navigation channel and the shoreline. A total of nine locations were placed at the navigation channel centerline, with spacing approximately 450 feet between each location (Figure 2 of the FSP). An additional 26 locations were located in pairs targeting both sides of the navigation channel. In general, proposed side slope sampling locations are spaced 450 feet apart and 40 feet from the navigation channel centerline location. Sediments will be analyzed for metals, PCBs, PAHs, and TOC and the results will be compared to proposed sediment screening criteria as provided in Table 2.	Most of the potential decision errors related to sample collection and analysis are typically associated with field and laboratory sample variability and sample collection procedures. QC procedures are incorporated into the field SOPs to minimize field sample collection error. Multiple sampling locations are included to account for field variability. Laboratory SOPs will be followed to minimize laboratory analysis error. Analytical error will be identified through validation. Data will be flagged, as appropriate, and any use restrictions will be noted. Reporting limit goals for sediment chemistry are presented in Table 2.	Details for the plan of obtaining the data associated with DQOs 1 through 5 are provided in Section 4 the FSP.
		DQO 2: Determine the vertical extent of contaminated sediment (metals, PAHs, and PCBs) in SMC area.	The MKE AOC boundary as depicted in Figure 1 of the FSP. Sampling will be focused in the SMC as shown in Figure 2 of the FSP.	Sediment cores at each of the 35 locations in the SMC will be advanced to native material (up to a maximum penetration depth of 20 feet), or until refusal. Sediment cores will be segmented into as many as 11 samples using the following segmentation scheme: • 0 to 1.0 feet below sediment surface • 1.0 to 2.5 feet below sediment surface • 2.5 to 4.0 feet below sediment surface • 4.0 to 6.0 feet below sediment surface • 6.0 to 8.0 feet below sediment surface • 8.0 to 10.0 feet below sediment surface • 10.0 to 12.0 feet below sediment surface • 12.0 to 14.0 feet below sediment surface • 14.0 to 16.0 feet below sediment surface • 16.0 to 18.0 feet below sediment surface • 18.0 to 20.0 feet below sediment surface Sediments will be analyzed for metals, PCBs, PAHs, and TOC and the results will be compared to proposed sediment screening criteria as provided in Table 2.	Most of the potential decision errors related to sample collection and analysis are typically associated with field and laboratory sample variability and sample collection procedures. QC procedures are incorporated into the field SOPs to minimize field sample collection error. Multiple sampling locations and sample depths are included to account for field variability. Laboratory SOPs will be followed to minimize laboratory analysis error. Analytical error will be identified through validation. Data will be flagged, as appropriate, and any use restrictions will be noted. Reporting limit goals for sediment chemistry are presented in Table 2.	

Table 6
Data Quality Objectives

DQO Component						
Step 1: State the Problem	**Step 2: Identify the Goal of the Study**	**Step 3: Identify the Information Inputs**	**Step 4: Define the Boundaries of the Study**	**Step 5: Develop the Analytical Approach**	**Step 6: Specify Performance or Acceptance Criteria**	**Step 7: Develop the Plan for Obtaining Data**
Previous sampling within the Milwaukee River Estuary Area of Concern (MKE AOC) has shown elevated levels of metals, PCBs, and PAHs in sediments of the SMC. Furthermore, sampling conducted by the USACE homogenized sediment over the entire core length to understand composition of dredged material. Finer resolution sampling within the SMC is needed to understand depths of contamination for future remedial decision making. To date, neither sediment nor surface water samples from the MKE AOC have been analyzed for PFAS.	Additional site characterization data are needed to properly assess the chemical and physical properties of the SMC to identify future areas of focus for further investigation or remediation. A PFAS Special Study is also needed to understand the presence of PFAS within the MKE AOC. Data obtained through this study will be used to assess future management option for the MKE AOC sediments.	**DQO 3:** Define the geotechnical engineering properties of sediment within the SMC to support remedial action evaluations.	The MKE AOC boundary as depicted in Figure 1 of the FSP. Sampling will be focused in the SMC as shown in Figure 2 of the FSP.	Sediment cores will be collected from four locations for analysis of moisture content, Atterberg limits, particle size, and specific gravity. The four locations were evenly spaced throughout the SMC at a frequency of 10% of the total locations. This number of samples is expected to be suitable in providing a representative physical characterization of sediments present in the SMC. Additionally, where fine-grained sediments (e.g., silts and clays) are observed within the core, strength parameters will be assessed using a pocket penetrometer and a torvane. Observed values of the compressive strength (pocket penetrometer) and shear strength (torvane) will be recorded. A minimum of one set of strength tests will be performed on a representative portion of sediment from a given depth interval.	Most of the potential decision errors related to sediment sample collection and analysis are typically associated with field and laboratory sample variability and sample collection procedures. QC procedures are incorporated into the field SOPs to minimize field sample collection error. Multiple locations and samples are included to account for field variability. Laboratory SOPs will be followed to minimize laboratory analysis error. Conducting the strength measurements using a properly calibrated device (pocket penetrometer or torvane) in accordance with the device manual will provide data of sufficient quality for the site characterization effort. The strength tests will be performed by an experienced engineer or geologist capable of recognizing erroneous data indicative of subsurface debris.	Details for the plan of obtaining the data associated with DQOs 1 through 5 are provided in Section 4 the FSP.
		DQO 4: Estimate phosphorus loading from surface sediment to water column within the SMC.	The MKE AOC boundary as depicted in Figure 1 of the FSP. Sampling will be focused in the SMC as shown in Figure 2 of the FSP.	Phosphorus testing within SMC will be performed on sediment and site water collected from three locations using direct-push sampling techniques (see Figure 2 from the FSP). Two of the three locations (SMC-19-13 and SMC-19-37) target side slopes or nearshore areas, while the third location (SMC-19-28) targets the main channel in an area of shoaling shown on the 2018 USACE bathymetric survey (see Figure 2 of FSP). Two cores will be collected from each of the three locations to provide a duplicate of each location.	The sediment cores for phosphorus testing will be accepted based on the sampling requirements provided by the Wisconsin State Laboratory of Hygiene. Sediment core acceptance criteria include: 1) each core will be no more than 3 feet in length, targeting approximately 30 inches of recovered surficial sediments; and 2) each core will be cut to contain 12 to 15 inches of headspace (i.e., not 100% full) to accommodate the phosphorus testing procedure. All laboratory analysis and data interpretation will be performed by the Wisconsin State Laboratory of Hygiene outside of this project. Conclusions may be incorporated into the Site Investigation Report, as appropriate.	

Table 6
Data Quality Objectives

DQO Component						
Step 1: State the Problem	**Step 2: Identify the Goal of the Study**	**Step 3: Identify the Information Inputs**	**Step 4: Define the Boundaries of the Study**	**Step 5: Develop the Analytical Approach**	**Step 6: Specify Performance or Acceptance Criteria**	**Step 7: Develop the Plan for Obtaining Data**
Previous sampling within the Milwaukee River Estuary Area of Concern (MKE AOC) has shown elevated levels of metals, PCBs, and PAHs in sediments of the SMC. Furthermore, sampling conducted by the USACE homogenized sediment over the entire core length to understand composition of dredged material. Finer resolution sampling within the SMC is needed to understand depths of contamination for future remedial decision making. To date, neither sediment nor surface water samples from the MKE AOC have been analyzed for PFAS.	Additional site characterization data are needed to properly assess the chemical and physical properties of the SMC to identify future areas of focus for further investigation or remediation. A PFAS Special Study is also needed to understand the presence of PFAS within the MKE AOC.	**DQO 5:** Document the presence, if any, of PFAS in sediments and surface within MKE AOC.	The MKE AOC boundary as depicted in Figure 1 of the FSP.	Sediment cores and surface water samples will be collected from 14 locations within the MKE AOC, focusing on six primary areas (Reach 4 of Milwaukee River, Reaches 4 and 5 of the Menomonee River including the SMC, Reaches 2 and 3 of the Kinnickinnic River including SkipperBud's slip, the confluence of the Milwaukee River, Kinnickinnic River, Inner Harbor, and Outer Harbor, Outer Harbor and Lake Michigan). Proposed locations within each of these areas were selected using a judgmental sampling design, taking into consideration: 1) existing chemical conditions in sediment; 2) the location of former industrial operations; 3) areas that may be identified for dredging in the future for navigational or remedial purposes; and 4) providing overall spatial coverage for the areas. Sediment cores at each location will be advanced to 4 feet, or until refusal. Sediment cores will be segmented into as many as four samples using the following segmentation scheme: • 0 to 0.5 feet below sediment surface • 0.5 to 1.0 feet below sediment surface • 1.0 to 2.0 feet below sediment surface • 2.0 to 4.0 feet below sediment surface Sediments will be analyzed for PFAS and TOC and surface water will be analyzed for PFAS and TSS. The results will be compared to PFAS screening levels to be compiled from other states.	As PFAS is found in many materials, screening field equipment, sample vessels, and personal items for potential sources of PFAS cross-contamination will be conducted prior to sampling. Most of the potential decision errors related to sample collection and analysis are typically associated with field and laboratory sample variability and sample collection procedures. QC procedures are incorporated into the field SOPs to minimize field sample collection error. Multiple locations and sample depths are included to account for field variability. Laboratory SOPs will be followed to minimize laboratory analysis error. Analytical error will be identified through validation. Data will be flagged, as appropriate, and any use restrictions will be noted. Reporting limit goals for sediment and water chemistry are presented in Table 3.	Details for the plan of obtaining the data associated with DQOs 1 through 5 are provided in Section 4 the FSP.

Notes:
Anchor QEA-Baird Joint Venture, 2019. *Field Sampling Plan*. Characterization of Sediments in South Menomonee Canal and Milwaukee AOC PFAS Sampling. Prepared for Wisconsin Department of Natural Resources. October 2019.
DQO: data quality objective
FSP: *Field Sampling Plan*
MKE AOC: Milwaukee River Estuary Area of Concern
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
PFAS: perfluoroalkyl and polyfluoroalkyl substances
QC: quality control
SMC: South Menomonee Canal
SOP: Standard Operating Procedure
TOC: total organic carbon
TSS: total suspended solids
USACE: U.S. Army Corps of Engineers

Table 7
Data Quality Criteria

Parameter	Precision	Accuracy[a]	Completeness
Sediment			
Geotechnical parameters	± 20% RPD	N/A	95%
Total solids	± 20% RPD	N/A	95%
TOC	± 25% RPD	75 – 125% R	95%
Metals	± 25% RPD	75 – 125% R	95%
PAHs	± 35% RPD	50 – 150% R	95%
PCBs	± 35% RPD	50 – 150% R	95%
PFAS	± 35% RPD	50 – 150% R	95%
Water			
TSS	± 20% RPD	N/A	95%
PFAS	± 30% RPD	50 – 150% R	95%

Notes:
a: Accuracy goals apply to laboratory control samples and matrix spike samples, as applicable to the analysis.
N/A: not applicable
R: recovery
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
PFAS: perfluoroalkyl and polyfluoroalkyl substances
RPD: relative percent difference
TOC: total organic carbon
TSS: total suspended solids

Table 8

Field and Laboratory Quality Control Sample Analysis Frequency

Analysis Type	Rinsate Blanks	Field Duplicates	Initial Calibration[a]	Ongoing Calibration	LCS	LD/MSD	Matrix Spikes	Method Blanks	Surrogate Spikes
Geotechnical parameters	NA	1 per 20 samples	Daily[b]	N/A	N/A	1 per 20 samples	N/A	N/A	N/A
TS/TSS	NA	1 per 20 samples	Daily[b]	N/A	N/A	1 per 20 samples	N/A	N/A	N/A
TOC	NA	1 per 20 samples	Daily	Every 10 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	N/A
Metals	1 per 20 samples	1 per 20 samples	Daily	Every 10 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	N/A
PCBs	1 per 20 samples	1 per 20 samples	As needed[c]	Every 20 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	Every sample
PAHs	1 per 20 samples	1 per 20 samples	As needed[c]	Every 12 hours	1 per 20 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	Every sample
PFAS	1 per 20 samples	1 per 20 samples	As needed[c]	Every 12 hours	1 per 20 samples	1 per 20 samples	1 per 20 samples	1 per 20 samples	Every sample

Notes:
a: Initial calibration verification and calibration blank must be analyzed after initial calibration and before samples are analyzed.
b: Calibration and certification of drying ovens and weighing scales are conducted bi-annually.
c: Initial calibrations are considered valid until the ongoing continuing calibration no longer meets method specifications. At that point, a new initial calibration is performed.
LCS: laboratory control sample
LD: laboratory duplicate
MSD: matrix spike duplicate
N/A: not applicable
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
PFAS: perfluoroalkyl and polyfluoroalkyl substances
TOC: total organic carbon
TS: total solid
TSS: total suspended solids

Table 9

Sample Containers, Holding Times, and Preservation

Parameter	Container Size and Type	Holding Time	Sample Preservation Technique
Sediment			
Grain size	16-oz glass or HDPE	6 months	Ambient
Atterberg limits		N/A	
Specific gravity		N/A	
Moisture content		N/A	
TS/TOC (CT Labs)	4-oz HDPE	28 days	< 6°C
Metals (except mercury)		6 months	
Mercury		28 days	
PAHs	4-oz glass	14 days to extraction	< 6°C
		40 days to analysis	
PCBs		14 days to extraction	
		40 days to analysis	
PFAS	8-oz HDPE	28 days	< 6°C
TOC (GEL Labs)	8-oz glass	28 days	< 6°C
Surface Water			
TSS	1-liter HDPE	7 days	2 to 6°C
PFAS	2 x 250 + 1 x 15 milliliter HDPE	14 days to extraction	< 10°C
		28 days to analysis	0 to 6°C

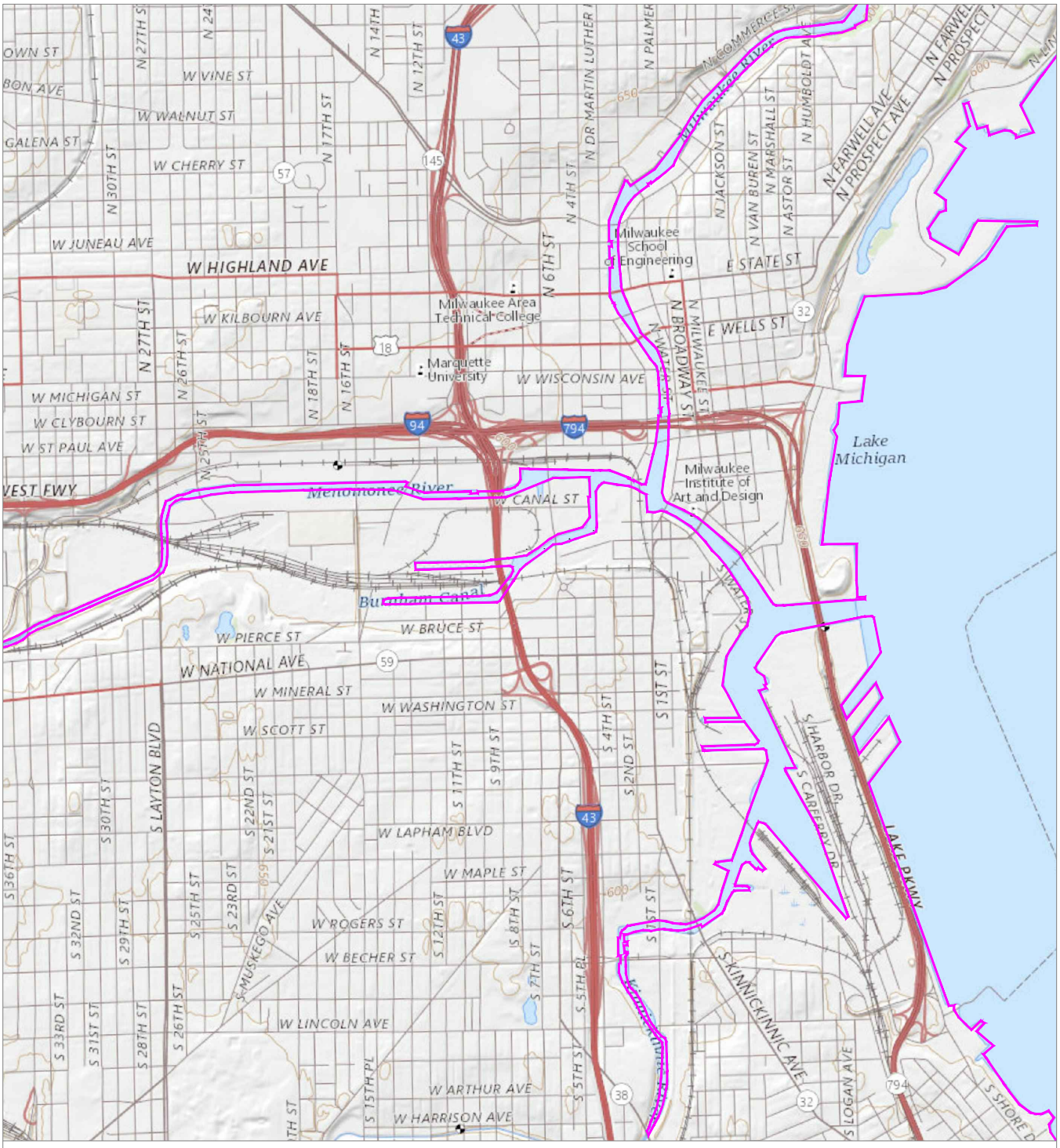
Notes:
HDPE: high-density polyethylene
N/A: not applicable
oz: ounce
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
PFAS: perfluoroalkyl and polyfluoroalkyl substances
TOC: total organic carbon
TS: total solid
TSS: total suspended solids

Table 10
Laboratory Addresses by Analysis Type

Laboratory	Laboratory Address	Sample Type	Analysis
CT Laboratories, LLC	CT Laboratories, LLC Attn: Sample Receiving 1230 Lange Court Baraboo, Wisconsin 53913	Sediment	Metals (arsenic, cadmium, chromium, copper, lead, nickel, zinc, and mercury), PAHs (TPAH-18), PCB Aroclors, and TOC
Eurofins TestAmerica	Eurofins TestAmerica Attn: Sample Receiving 30 Community DrSouth Burlington, Vermont 05403	Sediment	Geotechnical testing including grain size, Atterberg limits, specific gravity, and moisture content
GEL Laboratories, LLC	GEL Laboratories, LLC Attn: Sample Receiving 2040 Savage Road Charleston, South Carolina 29407	Sediment and Water	PFAS analyses (sediment and site water) TOC (sediment only) TSS analysis (site water only)
Wisconsin State Lab of Hygiene	Wisconsin State Lab of Hygiene Attn: Sample Receiving 2601 Agriculture Drive Madison, WI 53718	Sediment and Water	Phosphorus analyses (sediment and site water)

Notes:
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
PFAS: perfluoroalkyl and polyfluoroalkyl substances
TOC: total organic carbon
TPAH: total polycyclic aromatic hydrocarbon
TSS: total suspended solids

Figures



SOURCE: USGS Topographic Map

HORIZONTAL DATUM: Wisconsin State Plane, South Zone, North American Datum of 1983 (NAD83), U.S. Feet

LEGEND:

Milwaukee River Estuary AOC

0 3000

Feet

Publish Date: 2019/11/01 7:29 AM | User: bhurry
Filepath: K:\Projects\0000-Milwaukee\Milwaukee\Milwaukee AOC-RP-001 Location Figure.dwg Figure 1

ANCHOR QEA

Figure 1
Site Location Map

Milwaukee River Estuary Area of Concern
Milwaukee, Wisconsin

Attachment A
Laboratory Standard Operating Procedures

Title: Specific Gravity of Soil Solids by Water Pycnometer (ASTM D854-06 – Method B)

Approval Signatures:

Don Dawicki
Laboratory Director

Luke Orchard
Quality Assurance Manager

Matthew Kirk
Department Manager

Benjamin Kirchner
Health & Safety Coordinator

Approval Date: June 26, 2018

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure for the measurement of specific gravity in soils.

2.0 Summary of Method

A representative portion of sample passing a # 4 (4.75mm) sieve is weighed and placed in a calibrated volumetric flask to which reagent water is added. Specific gravity is determined by comparison of the density of water to the density of water + sample.

This SOP is based on the following reference methods:

> Method B of ASTM Standard D 854-06 "Standard Test Methods for Specific Gravity of Soils by Water Pycnometer". ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

If the laboratory has modified the procedure from the reference method(s) a list of modifications will be provided in Section 16.0.

3.0 Definitions

Specific Gravity of Soil Solids: The ratio of the mass of a unit volume of soil solids to the mass of the same volume of gass-free distilled water at 20℃.

4.0 Interferences

Soil Solids for this test method does not include solids which can be altered by this method (i.e. substances that would dissolve in water), contaminated with a substance that prohibits the use of this method, or are highly organic soil solids, such as fibrous matter which floats in water.

The term soil solids is typically assumed to mean naturally occurring mineral particles that are not readily soluble in water. Water-soluble solids such as lime or sodium chloride typically require special treatment. ASTM methods for special treatment are listed in ASTM D854-06 but are not currently offered by the laboratory. If laboratory analysis on such materials is desired, the laboratory recommends that procedures for treatment of samples and reporting specifications be specified by the customer prior to the start of analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

There are no materials with a health rating of 3 or 4 used in this procedure. A complete list of materials used in the method can be found in Section 7.0. If a chemical material is listed, employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Oven, 110°C (+/-5)
- Top loading balance
- Aluminum measuring pans
- Stainless steel spatulas and spoons
- Volumetric flask, 250 mL. (Pycnometer)
- Mortar and Rubber Tipped Pestle
- Thermometer (+/-0.5℃)
- Insulated container or large cooler
- No. 4 (4.75mm) sieve
- Funnel
- 400 mL glass beaker
- Hot Plate
- Disposable pipettes

7.0 Reagents and Standards

Reagent Water

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. Sample collection procedures are provided in this SOP for guidance only. The laboratory recommends that all samples be collected in accordance with a client specified sampling plan.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Solid	Glass	200g	4℃	NA	D854-06

Unless otherwise specified by client or regulatory program, after analysis samples are held for a minimum of 30 days and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Calibration and Standardization

Check the calibration of the balance on each day of use prior to use using at least 2 Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

The QA Manager or designee checks the calibration of liquid in glass thermometers annually against a NIST-traceable thermometer following the procedures given in laboratory SOP BR-QA-012 *Support Equipment Check*. Electronic / digital thermometers that are battery-operated are checked quarterly using the same procedure.

Calibrate the pycnometer annually or when the dry, empty mass is outside of 0.06 g of the average calibrated mass. The calibration procedure is provided in Appendix A of this SOP.

10.2 Sample Preparation

Dry enough sample to ensure at least 60 g of dried sample will pass the #4 (4.75mm) sieve. Dry the sample for 16 hours in an oven set at a temperature of 110°C then break up any soil aggregates formed during the drying process with a rubber-tipped pestle and mortar.

10.3 Sample Analysis (Method B)

Obtain a clean dry flask for each sample. Weigh the flask and record the measurement in the LIMS worksheet. The mass of the flask must be within 0.06 g of its previously averaged calibrated mass. If the mass is outside this range, re-calibrate the flask using the procedure given in Appendix A.

Place a funnel into the flask and transfer up to 60 g of sample to the flask.
Fill the flask with reagent water until the water level is between 1/2 and 1/3 of the depth of the main body of the flask. Agitate the flask until a slurry forms and rinse any soil that adheres to the side of the flask into the slurry.

Place a hot plate inside a fume hood and place the flask on the hot plate. Boil the sample slurry for at least 2 hours. Shake the flask vigorously several times throughout the boil to prevent the sample slurry from sticking. Use only enough heat to keep the slurry boiling. After 2 hours has elapsed, remove flask from the hot plate.

Fill the flask above the reference line with reagent water and let sample cool to room temperature. Place the flask into a cooler, along with a thermometer, a pipette and a bottle of reagent water. Close the cooler and allow the sample to thermally equilibrate for at least 16 hours. After thermal equilibrium, adjust the volume of the water in the flask to the calibration mark, taking care to avoid entrapment of air.

Tare the top loading balance and weigh the flask. Upload the weight measurement into the LIMS worksheet.
Using the thermally equilibrated thermometer, measure the temperature of the sample and water and enter the temperature reading in the LIMS worksheet.

Tare the balance and label and weigh a 400 mL glass beaker uploading the weight measurement into the LIMS worksheet. Transfer the soil and water from the flask to the beaker. To ensure a complete transfer rinse the flask with reagent water as needed.

Place the beaker in a drying oven and dry the soil and water for at least 16 hours at a temperature of 110°C +/- 5°. After this time period has passed, remove the 400 mL glass beaker from the oven and cool to room temperature.

Reweigh the beaker and upload the weight measurement into the LIMS worksheet.

The LIMS calculates the specific gravity using the equations given in Section 11.1. Porosity is calculated using the equation in appendix B.

11.0 Calculations / Data Reduction

11.1 Calculations

- Equation 1: Mass of pycnometer and water at the test temperature

  $M_{\rho w,t} = M_p + (V_p * \rho_{w,t})$

  Where:
  $M_{\rho w,t}$ = mass of the pycnometer and water at the test temperature (T_t), g.
  M_p = the average calibrated mass of the dry pycnometer, g.
  V_p = the average calibrated volume of the pycnometer, mL.
  $\rho_{w,t}$ = the density of water at the test temperature (T_t), g/mL from table 1.

- Equation 2: Specific gravity of soil solids at the test temperature, G_t

  $G_t = \rho_s/\rho_{w,t} = M_s/(M_{\rho w,t} – (M_{\rho ws,t} – M_s))$

  Where:
  ρ_s = the density of the soil solids Mg/m^3 or g/cm^3
  $\rho_{w,t}$ = the density of water at the test temperature (T_t), g/mL or g/cm^3 from table 1
  M_s = the mass of the oven dry soil solids, g.
  $M_{\rho ws,t}$ = the mass of the pycnometer, water, and soil solids at the test temperature (T_t), g.

- Equation 3: Specific gravity of soil solids at 20°C

  $G_{20°C} = K * G_t$

  Where:
  K = the temperature coefficient given in table 1.

11.2 Primary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Upload the batch information into LIMS and complete the batch editor and worksheet. Initiate NCMs for any anomalies observed during the preparation process. Set the status of the batch to 1st level review.

11.3 Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of the batch to second level review.

Review the batch, run QC checker as appropriate and set the status to lab complete.

11.4 Data Reporting

Sample results are reported from the laboratory's LIMS system using the formatter specified by the Project Manager.

11.5 Data Archival

Data are stored in the laboratory's LIMS system.

12.0 Method Performance

12.1 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations.

Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste Satellite Container: 5 Gallon Plastic Bucket.

15.0 References / Cross-References

- Method B of ASTM Standard D 854-06 “Standard Test Methods for Specific Gravity of Soils by Water Pycnometer”. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- Corporate Environmental Health and Safety Manual (CW-E-M-001)
- SOP BR-QA-012 Support Equipment Check.

16.0 Method Modifications

None

17.0 Attachments

- Density of Water and Temperature Coefficient (K) for Various Temperatures.
- Appendix A: Pycnometer Calibration Procedure
- Appendix B: Calculations for Porosity

18.0 Revision History

Revision 9:

- Title Page: Updated approval signatures and copyright date
- Section 10.1 & 15.0: Updated title of SOP BR-QA-012
- Section 10.3: minor typographical clarifications

Previous revisions are retained by the QA department.

Temperature (°C)	Density (g/mL)[B]	Temperature Coefficient (K)	Temperature (°C)	Density (g/mL)[B]	Temperature Coefficient (K)	Temperature (°C)	Density (g/mL)[B]	Temperature Coefficient (K)	Temperature (°C)	Density (g/mL)[B]	Temperature Coefficient (K)
15.0	0.99910	1.00090	16.0	0.99895	1.00074	17.0	0.99878	1.00057	18.0	0.99860	1.00039
.1	0.99909	1.00088	.1	0.99893	1.00072	.1	0.99876	1.00055	.1	0.99858	1.00037
.2	0.99907	1.00087	.2	0.99891	1.00071	.2	0.99874	1.00054	.2	0.99856	1.00035
.3	0.99906	1.00085	.3	0.99890	1.00069	.3	0.99872	1.00052	.3	0.99854	1.00034
.4	0.99904	1.00084	.4	0.99888	1.00067	.4	0.99871	1.00050	.4	0.99852	1.00032
.5	0.99902	1.00082	.5	0.99886	1.00066	.5	0.99869	1.00048	.5	0.99850	1.00030
.6	0.99901	1.00080	.6	0.99885	1.00064	.6	0.99867	1.00047	.6	0.99848	1.00028
.7	0.99899	1.00079	.7	0.99883	1.00062	.7	0.99865	1.00045	.7	0.99847	1.00026
.8	0.99898	1.00077	.8	0.99881	1.00061	.8	0.99863	1.00043	.8	0.99845	1.00024
.9	0.99896	1.00076	.9	0.99879	1.00059	.9	0.99862	1.00041	.9	0.99843	1.00022
19.0	0.99841	1.00020	20.0	0.99821	1.00000	21.0	0.99799	0.99979	22.0	0.99777	0.99957
.1	0.99839	1.00018	.1	0.99819	0.99998	.1	0.99797	0.99977	.1	0.99775	0.99954
.2	0.99837	1.00016	.2	0.99816	0.99996	.2	0.99795	0.99974	.2	0.99773	0.99952
.3	0.99835	1.00014	.3	0.99814	0.99994	.3	0.99793	0.99972	.3	0.99770	0.99950
.4	0.99833	1.00012	.4	0.99812	0.99992	.4	0.99791	0.99970	.4	0.99768	0.99947
.5	0.99831	1.00010	.5	0.99810	0.99990	.5	0.99789	0.99968	.5	0.99766	0.99945
.6	0.99829	1.00008	.6	0.99808	0.99987	.6	0.99786	0.99966	.6	0.99764	0.99943
.7	0.99827	1.00006	.7	0.99806	0.99985	.7	0.99784	0.99963	.7	0.99761	0.99940
.8	0.99825	1.00004	.8	0.99804	0.99983	.8	0.99782	0.99961	.8	0.99759	0.99938
.9	0.99823	1.00002	.9	0.99802	0.99981	.9	0.99780	0.99959	.9	0.99756	0.99936
23.0	0.99754	0.99933	24.0	0.99730	0.99909	25.0	0.99705	0.99884	26.0	0.99679	0.99858
.1	0.99752	0.99931	.1	0.99727	0.99907	.1	0.99702	0.99881	.1	0.99676	0.99855
.2	0.99749	0.99929	.2	0.99725	0.99904	.2	0.99700	0.99879	.2	0.99673	0.99852
.3	0.99747	0.99926	.3	0.99723	0.99902	.3	0.99697	0.99876	.3	0.99671	0.99850
.4	0.99745	0.99924	.4	0.99720	0.99899	.4	0.99694	0.99874	.4	0.99668	0.99847
.5	0.99742	0.99921	.5	0.99717	0.99897	.5	0.99692	0.99871	.5	0.99665	0.99844
.6	0.99740	0.99919	.6	0.99715	0.99894	.6	0.99689	0.99868	.6	0.99663	0.99842
.7	0.99737	0.99917	.7	0.99712	0.99892	.7	0.99687	0.99866	.7	0.99660	0.99839
.8	0.99735	0.99914	.8	0.99710	0.99889	.8	0.99684	0.99863	.8	0.99657	0.99836
.9	0.99732	0.99912	.9	0.99707	0.99887	.9	0.99681	0.99860	.9	0.99654	0.99833
27.0	0.99652	0.99831	28.0	0.99624	0.99803	29.0	0.99595	0.99774	30.0	0.99565	0.99744
.1	0.99649	0.99828	.1	0.99621	0.99800	.1	0.99592	0.99771	.1	0.99562	0.99741
.2	0.99646	0.99825	.2	0.99618	0.99797	.2	0.99589	0.99768	.2	0.99559	0.99738
.3	0.99643	0.99822	.3	0.99615	0.99794	.3	0.99586	0.99765	.3	0.99556	0.99735
.4	0.99641	0.99820	.4	0.99612	0.99791	.4	0.99583	0.99762	.4	0.99553	0.99732
.5	0.99638	0.99817	.5	0.99609	0.99788	.5	0.99580	0.99759	.5	0.99550	0.99729
.6	0.99635	0.99814	.6	0.99607	0.99785	.6	0.99577	0.99756	.6	0.99547	0.99726
.7	0.99632	0.99811	.7	0.99604	0.99783	.7	0.99574	0.99753	.7	0.99544	0.99723
.8	0.99629	0.99808	.8	0.99601	0.99780	.8	0.99571	0.99750	.8	0.99541	0.99720
.9	0.99627	0.99806	.9	0.99598	0.99777	.9	0.99568	0.99747	.9	0.99538	0.99716

[A]Reference: CRC Handbook of Chemistry and Physics, David R. Lide, Editor-in-Chief, 74th Edition, 1993–1994.
[B]mL = cm^3.

Appendix A: Pycnometer Calibration Check Procedure

Check the average mass of the pycnometer annually or when the measured mass is outside of 0.06g of the previous calibrated average mass.

Equipment & Supplies

- 250 mL volumetric flask
- Top loading balance
- RO water
- Thermometer
- Large cooler with lid
- Disposable pipettes

Procedure

Obtain a clean, dry flask and record the flask number in the Excel worksheet

Weigh the flask five times, recording the each weight measurements in the Excel worksheet as "Flask (g)"

Determine and record the average and standard deviation of the weight measurements. The standard deviation shall be less than or equal to 0.02g. If it is greater, attempt additional measurements or use a different balance.

Fill the flask to just above the calibration line with de-aired/de-ionized water taking care to not entrap air bubbles in the water.

Place the flask into the cooler, along with a thermometer, disposable pipettes and a bottle of deaired/deionized water.

Cover the cooler, and allow the flask and water to sit for at least three hours in order to reach thermal equilibrium.

Set the cooler next to a balance, and remove the cover.

Handling the flask only by the rim, remove and place the flask onto a block of Styrofoam.

Using the thermally equilibrated pipette, adjust the volume of the water in the flask to the calibration mark, taking care to avoid entrapment of air.

Check for and remove any water beads on the pycnometer stem or on the exterior of the flask.

Measure and record the mass of the pycnometer and water to the nearest 0.01g.

Using the thermally equilibrated thermometer, measure and record the temperature of the flask to the nearest 0.1°C.

Repeat steps 3 through 11 to obtain five independent measurements on each pycnometer.

Calculate the average and standard deviation of the five volume determinations. If the standard

deviation is greater than 0.05mL, discard the results and repeat the procedure.

Determine the calibrated volume of the pycnometer using the following equation:

$$V_p = \frac{(M_{pw,c} - M_p)}{\rho_{w,c}}$$

Where:

V_p = the calibrated volume of the pycnometer, mL.

$M_{pw,c}$ = the mass of the pycnometer and water at the calibration temperature, g.

M_p = the average mass of the dry pycnometer at calibration, g.

$\rho_{w,c}$ = the mass density of water at the calibration temperature g/mL, (Table 1)

Appendix B: Porosity Calculation

Porosity is calculated using the sample's determined Specific Gravity and In Place Density. The calculation is as follows:

n = 100 [1-(pb/pd)]

Where:

n = porosity in %
pb = bulk density of the sediment in g/cm^3
pd = particle density in g/cm^3

Fetter, C.W. 2001. Applied Hydrogeology. Prentice Hall, Upper Saddle River, NJ. on p. 70. Book has 598 p.

Title: Particle Size Analysis (ASTM D 2217 and D422-63)

Approval Signatures:

Don Dawicki
Laboratory Director

Kristine Dusablon
Quality Assurance Manager

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Dept. Supervisor

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Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of particle size distribution in soils.

2.0 Summary of Method

A portion of sample is soaked in a dispersing agent then partitioned into separate portions: material retained on a #10 sieve and material passing the #10 sieve. The material retained on the #10 sieve is dried to constant weight then passed through a large size sieve stack; the material retained on each sieve is measured and recorded. Material passing the #10 sieve is subject to hydrometer analysis then passed through a small size sieve stack; the material retained on each sieve is measured and recorded. All measurements: large and small sieves and hydrometer readings, and the hygroscopic moisture are used to establish the particle size distribution of the sample.

This SOP is based on the following reference methods:

- ASTM Standard D 2217 – 85 (Re-approved 1998) "Standard Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

- ASTM Standard D 422-63 (Rapproved 2007) "Standard Test Method for Particle-Size Analysis of Soils", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

NOTE: ASTM D2217 was withdrawn without replacement by ASTM in 2007. A withdrawn standard is an ASTM standard that has been discontinued by the ASTM Sponsoring Committee responsible for the standard.
ASTM D422-63 was withdrawn by ASTM in January 2016

If the laboratory has modified the procedure from the reference method(s) a list of modifications will be provided in Section 16.0.

3.0 Definitions

Not Applicable

4.0 Interferences

Not Applicable

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples

and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Not Applicable

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Top-Loading Balance, capable of weight measurement to 0.01 g
- Mechanical Stirring Device and Dispersion Cup
- Thermometer: Accurate to 0.5°C
- Mortar and Rubber Tipped Pestle
- Sedimentation Cylinder(s) 1000 mL
- Hydrometer: ASTM 151H in specification E 100.
- Sieves, of the following size(s): Gilson Company, Inc. or equivalent
  3.0” (75.00 mm)
  2.0” (50.00 mm)
  1.5” (37.50 mm)
  1.0” (25.00 mm)
  3/4" (19.00 mm)
  3/8” (9.50 mm)
  # 4 (4.75 mm)
  #10 (2.00 mm)
  #20 (850.0 um)
  #40 (425 um)
  #60 (250.0 um)
  #80 (180.0 um)
  #100 (150.0 um)
  #200 (75.0 um)
- Drying Oven with temperature range of 60-110°C
- Stainless Steel Spatulas & Spoons
- Metal & Bristle Brushes
- Ro-Tap Sieve Shaker, W. S. Tyler or equivalent.
- Timing Device with second hand and capable of counting up to 25 hours

7.0 Reagents and Standards

- Reverse Osmosis (RO) water: In-House System
- Sodium Hexametaphosphate: ELE International or equivalent.

Sodium Hexametaphosphate Solution: Add 120 g of sodium hexametaphosphate and 2940 g of reagent water to a 1-gallon bottle. Add a stir rod to the container and place on a stir plate. Mix the solution until it is homogeneous. Assign an expiration date of 30 days from the date made unless the parent reagent expires sooner, in which case use the earlier expiration date. Store the prepared solution at ambient temperature.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection, so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation, and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Solid	Glass Jar w/ Teflon Lid	500 g	None	None	ASTM D422-63

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Equipment Calibration

Check the calibration of the balance prior to use, using at least two Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

NOTE: The QA Manager or their designee checks the calibration of liquid in glass thermometers annually against a NIST-traceable thermometer following the procedures given in laboratory SOP BR-QA-004. Electronic / digital thermometers that are battery-operated are checked quarterly using the same procedure.

Calibrate the hydrometers every two years following the procedure given in BR-GT-008.

Calibrate the sieves six months following the procedure given in BR-GT-008.

10.2 Hygroscopic Moisture Determination

Label an aluminum pan with the Lab ID for each sample. Tare the balance, weigh each pan, and record the weight measurement in spreadsheet FSL024.

Mix the sample with a stainless steel spatula. Measure at least 10-15 g of each sample into the labeled aluminum pan and record the weight of sample in the spreadsheet.

Place the pan + sample in an oven maintained at a temperature of 110ºC and dry the sample for at least 16 hours. Reweigh each pan and record the weight measurement in the spreadsheet.

Percent solids are calculated using the equation given in Section 11.0.

10.3 Sample Preparation

Use the calculated percent solids and the sample characteristics for each sample to determine the amount needed for analysis. The target mass for dry clay samples is ~60g of material, and for dry sandy/gravel material the target mass is ~125g. For very wet samples (lower %Solids), use a larger sample mass. See Table 2 for guidance on sample masses. If there is an insufficient amount of sample available, initiate a nonconformance memo (NCM) and contact the PM for further instruction.

Place a 1000 mL plastic beaker on the balance and enter the weight measurement in the worksheet as the tare weight. Weigh the amount of sample for analysis and record the weight in the bench sheet.

Add 125 mL of sodium hexametaphosphate solution to each beaker. Stir to mix and soak the sample in this solution for 16 hours

10.4 Sample Partition

Rinse the sample slurry into a dispersion vessel using reagent water. Fill the dispersion vessel ½ full with reagent water and disaggregate well using a combination of agitation and homogenization.

NOTE: If the sample is not amenable to disaggregation, initiate a NCM to notify the PM of the anomaly and proceed to the next step without dispersing the sample.

Place a #10 sieve in a funnel above a 1000 mL graduated cylinder. Pour the sample through the sieve. Rinse the dispersion vessel with reagent water and pour the rinse through the sieve. Repeat until transfer is complete. Bring the volume in the graduated cylinder to 1000 mL with reagent water. Cover the cylinder with a rubber stopper and equilibrate the sample to ambient temperature in preparation for hydrometer analysis.

Label a medium size aluminum dish with the sample's LAB ID, then transfer the sample material that was retained on the #10 sieve to the dish. Place the aluminum dish in the drying oven set at 110 ± 5° C and dry the sample material for at least 16 hours or until constant weight. Set aside for sieve analysis.

10.5 Hydrometer Analysis

Prepare a hydrometer rinse bath by adding 1000 mL of reagent water to a 1000 mL graduated cylinder.

Record the hydrometer ID and start time on the worksheet. Set the timer for the elapsed time and perform each task as listed in Table 1: Hydrometer Reading Table.

To shake the cylinder, rotate the flask up and down for one minute approximating at least 60 turns. One turn down and one turn up equals two turns.

To take a hydrometer reading, gently insert the hydrometer into the graduated cylinder and wait ~ 20 seconds. Read the hydrometer from the top of the meniscus to the nearest 0.0005. Enter the reading on the worksheet. After each reading, clean the hydrometer by twisting and dropping the hydrometer into the hydrometer rinse bath.

Insert a temperature probe into the cylinder to the same depth as the hydrometer reading. Read the temperature to the nearest 0.5°C and enter the temperature measurement on the worksheet. Rinse the temperature probe in the hydrometer rinse bath.

Repeat the above process taking hydrometer readings every 2, 5, 15, 30, 60, 250 and 1440 minutes as per Table 1 then proceed to small sieve analysis.

10.6 Sieve Analysis

Inspect the sample material in the aluminum pan and record a description of the non-soil material (e.g.- sticks, grass, wood, plastic), hardness of material, and shape of material in the worksheet.

Hardness qualifiers include hard, soft, and brittle. Shape qualifiers include well rounded, rounded, subrounded, subangular, and angular.

Large Sieves

Weigh the 3/4", 3/8", #4 and #10 sieves and enter the weight measurements in the worksheet as the tare weight.

Stack the sieves and then transfer the sample material from the aluminum dish to the sieve stack. If the sample material is less than 30 g, manually shake the sieve stack for 2 minutes. If the sample material is greater than 30 g, place the sieve stack into the Ro-tap machine and shake the sieve stack for 10 minutes.

Weigh each sieve and record these measurements in the worksheet.

Small Sieves

Quantitatively transfer the sample from the graduated cylinder to a #200 wet wash sieve. Ensure the entire sample has been transferred to the #200 wet wash sieve by rinsing the graduated cylinder several time with RO water. Using RO water, wash the sample through the #200 sieve until the water runs clear, then transfer the material retained on the sieve into a 250 mL glass beaker labeled with the sample's LAB ID.

Place the beaker in the drying oven and dry at a temperature of 110ºC for at least 16 hours. After 16 hours, remove the beaker from the oven and allow it to cool.

Gently mix the dried contents of the beaker with a rubber-tipped pestle to break up any soil aggregates that may have formed during the drying stage.

Tare the balance and weigh the sieve stack sized between #20 and #200 and record the tare weights.

Transfer the sample to the sieve stack and ensure complete transfer. Use hair or wire brushes to clean the beaker. Place the sieve stack on the RoTap machine and shake for ten minutes.

Weigh each sieve and record these measurements in the worksheet.

11.0 Calculations / Data Reduction

11.1 Calculations

Sample Used (SU): Dry Preparation

$$SU = (pan + dry\ sample - pan) - (pan + non - soil\ material - pan) \otimes HMCF$$

Where:
HMCF = Hygroscopic moisture correction factor.

Sieve Analysis (Percent Finer = PF)

Large Sieves:

3 inch: PF = 100-100 (Sieve and Sample (3 inch) - Sieve (3 inch))/SU*

2 inch: PF = PF (3 inch) - 100(Sieve and Sample (2 inch) - Sieve (2 inch))/SU and so on through the #10 Sieve.*

Small Sieves:

#20: PF = PF(#10) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#20) - sieve(#20))/sample used*

#40: PF = PF (#20) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#40) - sieve (#40))/sample used and so on up through #10 sieve.*

Hydrometer Analysis

Particle size, Micron

1000*sqrt [930*viscosity/980*(SG-1))*(effective depth/time)]

Viscosity at sample temperature, poises
Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading - 1) above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-

67.0/27.8)+10.5 and 264.5 = (10.5-2.3)/0.031
Time, minutes = Time of hydrometer reading from beginning of sedimentation
Sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow
Percent Finer (PF):

PF = Constant*(actual hydrometer reading - hydrometer correction factor - 1)

Where:
Constant = (100,000/W)*SG/(SG-1)
W = (Total sample used *sample used for hydrometer analysis*HMCF)/Amount of total sample passing #10 sieve
Hydrometer Correction = slope*sample temperature + Intercept
Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))
Intercept = (low temp. reading -1) - (low temp. * slope)

11.2 Data Reduction

11.2.1 Primary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Upload the batch information into LIMS and complete the batch editor and worksheet. Initiate NCMs for any anomalies observed during the preparation process. Set the status of the batch to 1st level review.

11.2.2 Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of the batch to second level review.

11.2.3 Lab Complete

Review the batch, run QC checker as appropriate and set the status to lab complete.

11.2.4 Data Reporting

Sample results are reported from the laboratory's LIMS system using the formatter specified by the Project Manager.

11.2.5 Data Archival

Data are stored in the laboratory's LIMS system.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

This section is not applicable to this procedure.

12.2 Demonstration of Capabilities (DOC)

Analyze a sample in quadruplicate as a demonstration of capability initially on learning the procedure and annually thereafter. Use FQA053 to document results and verify if DOC meets acceptance criteria.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste-Satellite Container: Solid Waste 5 Gallon Plastic Bucket (inside fume hood)
- Liquid Waste- 55 gallon poly drum

15.0 References / Cross-References

- ASTM Standard D 2217 – 85 (Re-approved 1998) "Standard Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

- ASTM Standard D 422-63 (Re-approved 2007) "Standard Test Method for Particle-Size Analysis of Soils", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

Note: ASTM D2217 was withdrawn without replacement by ASTM in 2007. A withdrawn standard is an ASTM standard that has been discontinued by the ASTM Sponsoring Committee responsible for the standard.
ASTM D422-63 was withdrawn by ASTM in January 2016

16.0 Method Modifications

- The laboratory prepares samples for ASTM D422 using ASTM method D2217 rather then the suggested method ASTM D421.
- The laboratory does not use Apparatus A or B defined in ASTM D422-63 for dispersion of samples due to the difficulty that many samples present using apparatus A and the unavailability of apparatus B. Instead the laboratory manually disaggregates the samples.

17.0 Attachments

- Table 1: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)
- Table 2: Percent Solids Table for Weight Determination for D422.

18.0 Revision History

BR-GT-006, Revision 8.1:
- Title Page: Updated approval signatures, Copyright info, branding, and Dates.
- Section 10.3: added guidance for visual evaluation of sample for mass to use.

Previous revisions are retained by the QA department

Table 1: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)

Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)	Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)
0:00	Shake	1		1:01	Read	10	5
0:01	**Place**	**1**		**1:02**	Shake	11	
0:01	**Shake**	**2**		**1:03**	Place	11	
0:02	Place	2		1:04	Read	9	15
0:03	Read	1	2	1:05	Read	11	2
0:04	Read	2	2	1:06	Read	7	31
0:06	Read	1	5	1:07	Read	3	58
0:07	Read	2	5	1:08	Read	11	5
0:08	Shake	3		**1:09**	Shake	12	
0:09	**Place**	**3**		**1:10**	Place	12	
0:09	**Shake**	**4**		1:11	Read	10	15
0:10	Place	4		1:12	Read	12	2
0:11	Read	3	2	1:13	Read	4	63
0:12	Read	4	2	1:14	Read	8	32
0:14	Read	3	5	1:15	Read	12	5
0:15	Read	4	5	1:18	Read	11	15
0:16	Read	1	15	1:19	Read	9	30
0:17	Read	2	15	1:21	Read	5	60
0:20	Shake	5		1:25	Read	12	15
0:21	Place	5		1:26	Read	10	30
0:23	Read	5	2	1:27	Read	6	59
0:24	Read	3	15	1:33	Read	11	30
0:25	Read	4	15	1:34	Read	7	59
0:26	Read	5	5	1:41	Read	12	31
0:27	Shake	6		1:42	Read	8	60
0:28	Place	6		1:52	Read	9	63
0:30	Read	6	2	1:53	Read	10	57
0:31	Read	1	30	2:06	Read	11	63
0:32	Read	2	30	2:07	Read	12	57
0:33	Read	6	5	4:17	Read	1	256
0:34	Shake	7		4:18	Read	2	256
0:35	Place	7		4:19	Read	3	250
0:36	Read	5	15	4:20	Read	4	250
0:37	Read	7	2	4:21	Read	5	240
0:38	Read	3	29	4:22	Read	6	234
0:39	Read	4	29	5:00	Read	7	265
0:40	Read	7	5	5:01	Read	8	259
0:41	Shake	8		5:02	Read	9	253
0:42	Place	8		5:03	Read	10	247
0:43	Read	6	15	5:04	Read	11	241
0:44	Read	8	2	5:05	Read	12	235
0:47	Read	8	5	24:01	Read	1	1440
0:48	Shake	9		24:02	Read	2	1440
0:49	Place	9		24:03	Read	3	1434
0:50	Read	7	15	24:04	Read	4	1434
0:51	Read	9	2	24:05	Read	5	1424
0:52	Read	5	31	24:06	Read	6	1418
0:54	Read	9	5	24:07	Read	7	1412
0:55	Shake	10		24:08	Read	8	1406
0:56	Place	10		24:09	Read	9	1400
0:57	Read	8	15	24:10	Read	10	1394
0:58	Read	10	2	24:11	Read	11	1388
0:59	Read	6	31	24:12	Read	12	1382
1:00	**Read**	**1**	**59**				
1:00	**Read**	**2**	**58**				

Source: Laboratory Prepared Reference Document

Table 2: Percent Solids Table for Weight Determination for D422.

Percent Solid Table

Quantities of sample (in grams) to be utilized in Wet method version of ASTM D854 and D422

% Sol	Spec Grav	Hydrometer Slt/Cl	Slt/Snd	Snd	Snd/Gr
	25	**50**	**75**	**100**	**200**
1	2500	5000	7500	10000	20000
2	1250	2500	3750	5000	10000
3	833	1667	2500	3333	6667
4	625	1250	1875	2500	5000
5	500	1000	1500	2000	4000
6	417	833	1250	1667	3333
7	357	714	1071	1429	2857
8	313	625	938	1250	2500
9	278	556	833	1111	2222
10	250	500	750	1000	2000
11	227	455	682	909	1818
12	208	417	625	833	1667
13	192	385	577	769	1538
14	179	357	536	714	1429
15	167	333	500	667	1333
16	156	313	469	625	1250
17	147	294	441	588	1176
18	139	278	417	556	1111
19	132	263	395	526	1053
20	125	250	375	500	1000
21	119	238	357	476	952
22	114	227	341	455	909
23	109	217	326	435	870
24	104	208	313	417	833
25	100	200	300	400	800
26	96	192	288	385	769
27	93	185	278	370	741
28	89	179	268	357	714
29	86	172	259	345	690
30	83	167	250	333	667
31	81	161	242	323	645
32	78	156	234	313	625
33	76	152	227	303	606
34	74	147	221	294	588
35	71	143	214	286	571
36	69	139	208	278	556
37	68	135	203	270	541
38	66	132	197	263	526
39	64	128	192	256	513
40	63	125	188	250	500
41	61	122	183	244	488
42	60	119	179	238	476
43	58	116	174	233	465
44	57	114	170	227	455
45	56	111	167	222	444
46	54	109	163	217	435
47	53	106	160	213	426
48	52	104	156	208	417
49	51	102	153	204	408
50	50	100	150	200	400

% Sol	Spec Grav	Hydrometer Slt/Cl	Slt/Snd	Snd	Snd/Gr
	25	**50**	**75**	**100**	**200**
51	49	98	147	196	392
52	48	96	144	192	385
53	47	94	142	189	377
54	46	93	139	185	370
55	45	91	136	182	364
56	45	89	134	179	357
57	44	88	132	175	351
58	43	86	129	172	345
59	42	85	127	169	339
60	42	83	125	167	333
61	41	82	123	164	328
62	40	81	121	161	323
63	40	79	119	159	317
64	39	78	117	156	313
65	38	77	115	154	308
66	38	76	114	152	303
67	37	75	112	149	299
68	37	74	110	147	294
69	36	72	109	145	290
70	36	71	107	143	286
71	35	70	106	141	282
72	35	69	104	139	278
73	34	68	103	137	274
74	34	68	101	135	270
75	33	67	100	133	267
76	33	66	99	132	263
77	32	65	97	130	260
78	32	64	96	128	256
79	32	63	95	127	253
80	31	63	94	125	250
81	31	62	93	123	247
82	30	61	91	122	244
83	30	60	90	120	241
84	30	60	89	119	238
85	29	59	88	118	235
86	29	58	87	116	233
87	29	57	86	115	230
88	28	57	85	114	227
89	28	56	84	112	225
90	28	56	83	111	222
91	27	55	82	110	220
92	27	54	82	109	217
93	27	54	81	108	215
94	27	53	80	106	213
95	26	53	79	105	211
96	26	52	78	104	208
97	26	52	77	103	206
98	26	51	77	102	204
99	25	51	76	101	202
100	25	50	75	100	200

Title: Liquid Limit, Plastic Limit & Plasticity of Soils (ASTM D4318- 05)

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Facility Distribution No. Electronic **Distributed To: Facility Intranet**

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1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of liquid limit, plastic limit and plasticity index of soils. This analysis is amenable to soils with significant amounts of silt and clay particles. It is not recommended for coarse-grained or sandy soils.

- Samples containing few to no particles that will be retained by #40 sieve are prepared using the wet preparation method.
- Samples containing a large percentage of particles that would be retained on a #40 sieve are prepared using the dry preparation method.

2.0 Summary of Method

Wet Preparation: A 150 to 200 g representative portion of sample that would pass through the #40 (425 um) sieve is spread into the brass cup of a mechanical liquid limit device and divided in two parts with a groove tool. The cup is repeatedly lifted and dropped until 13 mm (½ in.) of the sample flows together. This test is repeated several times at different water contents. The plastic limit is determined by repeatedly pressing the soil into an ellipsoidal shape and then rolling the soil into a 3.2 mm (1/8 inch) diameter thread, until the thread crumbles and sample can no longer be rolled into a ball or thread. The water content of the soil at this point is considered the plastic limit. The plasticity index is calculated as the difference between the liquid and plastic limits.

Dry Preparation: A representative portion of the sample is dried, pulverized and passed though a #40 sieve and placed in a mixing dish. The material retained on the #40 sieve is soaked with reagent water to separate the fine particles from coarse particles, decanted through a #40 sieve and collected in collection pan. The rinse water is added to the dried material which passed the #40 sieve and mixed with more reagent water to get to the proper liquid limit. A portion of the sample is spread into the brass cup of a mechanical liquid limit device and divided in two parts with a groove tool. The cup is repeatedly lifted and dropped until 13 mm (½ in.) of the sample flows together. This test is repeated several times at different water contents. The plastic limit is determined by repeatedly pressing the soil into an ellipsoidal shape and then rolling the soil into a 3.2 mm (1/8 inch) diameter thread, until the thread crumbles and sample can no longer be rolled into a ball or thread. The water content of the soil at this point is considered the plastic limit. The plasticity index is calculated as the difference between the liquid and plastic limits.

This SOP is based on the following reference methods:

- ASTM Standard D 4318-05 “Standard Test Methods for Liquid Limit, Plastic Limit and Plasticity Index of Soils”. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

If the laboratory has modified the procedure from the reference method(s) a list of modifications will be provided in Section 16.0.

3.0 Definitions

Atterberg Limits: Liquid limit and plastic limit of soils.

4.0 Interferences

Not Applicable

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Not applicable.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Oven, 110°C (+/-5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum measuring pans, Fisher Scientific or equivalent.
- Stainless steel spatulas and spoons, Fisher Scientific or equivalent.
- Heat shield gloves / Oven Tongs, Fisher Scientific or equivalent.
- 250 mL glass beakers
- Liquid limit device meeting the requirements of ASTM D4318
- Metal gauge block for calibration of liquid limit device
- Flat grooving tool meeting the requirements of ASTM D4318
- Frosted glass plate that is 12 inches square and 3/8 inch thick
- #40 (425um) sieve and collection pan
- Aluminum pans with close-fitting lids
- Parafilm
- Rubber-tipped pestle and mortar

7.0 Reagents and Standards

Reagent Water

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. Sample collection procedures are provided in this SOP for guidance only. The laboratory recommends that all samples be collected in accordance with a client specified sampling plan.

Listed below are recommended sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Solid	Glass	500g	None	None	Method

Unless otherwise specified by client or regulatory program, after analysis samples are held for a minimum of 30 days and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Calibration and Standardization

Check the calibration of the balance on each day of use prior to use using at least 2 Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

10.1.1 Liquid Limit Device Calibration Check

Liquid Limit Devices are purchased certified annually.

10.1.2 Grooving Tool Critical Dimension(s) Check

The groove tool is checked daily prior to use using the metal groove calibration tool.

10.2 Liquid Limit Procedure

10.2.1 Sample Preparation for Material that Passes the #40 Sieve (Wet Preparation)

Determine by visual and manual methods that the material has few to no particles that would be retained on the #40 sieve. In this case the samples will be processed using the wet preparation method. If the sample has a large percentage of material that will be retained on a #40 sieve the laboratory will prepare the sample using the dry preparation method described in Section 10.2.2.

For wet preparation prepare 150 to 200g of sample by mixing thoroughly with reagent water on a glass plate or mixing dish using a spatula. If needed, the sample can be soaked in a mixing dish with a small amount of reagent water to soften the material before mixing. Adjust the water content of the material to bring it to a consistency that would require 25-35 blows of the liquid limit device to close the groove. If during mixing, a small percentage of material is encountered that would be retained on the #40 sieve remove these particles by hand. Place the prepared material in the mixing dish and cover with parafilm, allow the material to stand for a minimum of 16 hours. Before starting the test thoroughly remix the sample. Proceed to Section 10.2.3.

10.2.2 Sample Preparation for Material Retained on the #40 Sieve (Dry Preparation)

Determine by visual and manual methods that the material has particles that would be retained on the #40 sieve. In this case, the laboratory's default method is dry preparation.

Dry a representative portion of the sample at room temperature until soil clods will pulverize easily. Once dry in appearance pulverize the sample using a rubber-tipped pestle and mortar being sure not to breakdown individual particles. Sieve the dried material through a #40 sieve collecting the material passing the sieve. Place all material passing the #40 sieve into a mixing dish. When large coarse particles such as shells, concretions or other fragile particles are found during pulverization do not crush these particles to make them pass the #40 sieve.

Place any material retained on the #40 sieve in an aluminum dish and soak with reagent water. Stir this material to separate the fine material from the coarse material. Transfer the sample and water mixture to a #40 sieve with a collection pan being sure to capture the water and any suspended fines in the collection pan. Discard the material retained on the #40 sieve. Pour the water mixture from the collection pan into the mixing dish containing the material that passed through the #40 sieve.

Adjust the water content of the mixture by adding small increments of reagent water or by allowing the mixture to dry at room temperature while mixing on a glass plate. The material should be at a water content that would require 25-35 blows of the liquid limit device to close the groove. Place the prepared material in the mixing dish and cover with parafilm, allow the material to stand for a minimum of 16 hours. Before starting the test thoroughly remix the sample. Proceed to Section 10.2.3.

10.2.3 Analysis (Method A)

Place a portion of the sample in the cup of the liquid limit device, press, pat and spread the sample until it reaches a depth of approximately 10mm at its deepest point, tapering to form a horizontal surface. Take care to work air bubbles out of the sample, but try to form the soil pat using as few strokes as possible. Cover any unused soil in the beaker to retain moisture.

Form a groove in the sample by drawing the tool, beveled edge forward, through the soil on a line joining the highest point to the lowest point on the rim of the cup. When cutting the groove, hold the tool against the surface of the cup and draw in an arc, maintaining the tool perpendicular to the surface of the cup. If the soil cannot be cut without tearing, use several shorter strokes of the grooving tool, or cut a slightly smaller groove using a spatula and use the grooving tool to form the final dimensions. Use extreme care to prevent the soil pat from sliding in the cup.

Clean the underside of the cup and verify that there are no soil crumbs present on the base or cup. Lift and drop the cup by turning the crank at a rate of 2 drops per second, until the two

halves of soil come in contact across the groove along a distance of 13mm (1/2”).

Verify that an air bubble has not caused premature closing of the groove by comparing both sides of the groove. Both sides of the groove should flow together with approximately the same shape. If an air bubble is present, add a small amount of soil to the sample in the cup, reform the soil and repeat the groove. If the soil slides on the surface of the cup, repeat the test with a higher water content. If after several attempts at higher water contents, the soil continues to slide in the cup or the number of blows to close the groove is always below 25, the liquid limit cannot be determined. When the liquid limit can not be determined record 0 for Liquid Limits and Plastic Limits in the Laboratory Information Management System (TALS) worksheet and create a non conformance memo (NCM).

Record the number of blows that it took to close the groove in the TALS worksheet.

Label a small aluminum pan for each sample. Place the pan on a tared balance and upload the weight measurement into the TALS worksheet.

Remove a section of sample approximately the width of the spatula, crossing the closure of the groove, and place it into the pre-weighed aluminum pan. Upload the weight measurement of pan + sample into the TALS worksheet.

Transfer the soil that remains in the cup back to the 250 mL beaker then wash and dry the cup, grooving tool and spatula.

Remix the sample and repeat the analysis at three different water contents. The trials should be set such that closure is achieved with 15 to 25 blows (1 Trial), 20 to 30 blows (2nd Trial) and 25 to 35 (3rd Trial).

When the trials are complete, determine the water content of the soil. To do so, place the aluminum pans + sample in the oven and dry for at least 16 hours at a temperature of 105ºC. Reweigh each pan and upload the weight measurements into the TALS worksheet.

Calculate the liquid limit using the equation given in Section 11.0.

10.3 Plastic Limit – Hand Method

Select ~20 g from the sample material that was prepared for the liquid limit test. Reduce the water content of the sample so it can be rolled without sticking to the hands by spreading the sample aliquot onto a frosted glass plate.

Take a 1.5 – 2.0 g portion of sample and form into an ellipsoidal mass. Using your fingertips and the glass plate quickly roll the mass into a thread of uniform diameter then continue rolling to reduce the diameter to 3.2mm (1/8”) taking no more than two minutes to do so.

Break the thread into several smaller pieces, reform the pieces into ellipsoidal masses, and re-roll into 3.2mm threads. Continue forming and rolling until the thread crumbles under the pressure for rolling and the soil can no longer be formed into a 3.2mm thread.

Label an aluminum pan with its close-fitting lid for each sample. Place the pan on the balance and upload the weight measurement to the TALS worksheet.

Gather the portions of the crumbled thread together and place it in the pan then immediately cover the pan.

Select another 1.5-2.0 g portion of the sample and repeat the previous steps until the covered aluminum pan contains at least 6 grams. Upload the final weight into the TALS worksheet.

Repeat the above steps to generate a second covered pan containing at least 6 g of soil.

Place both pans into the oven and dry for at least 16 hours. Once dry, re-weigh each pan and upload the weight measurements into the TALS worksheet.

If Plasticity Limits can not be determined record Non-Plastic in the TALS worksheet.

Calculate the plastic limit and plasticity index using the equations given in Section 11.0.

11.0 Calculations

- Liquid Limit (LL)

  $LL = W^n(N/25)^{0.121}$

  Plot the relationship between the water content (Wn) and the corresponding number of drops (N) on a semi-logarithmic scale. The water content (Wn) is plotted on the X-axis with an arithmetical scale, and the number of blows (N) is plotted on the Y-axis with a logarithmic scale. Draw the best straight line through three or more points. Take the water content that corresponds with 25 drops as the liquid limit.

- Plastic Limit (PL)

  Compute the average of the two water contents.

  $PL = (Wc_1+Wc_2)/2$

  Where:

  PL = plastic limit
  Wc_1 = water content of first trial
  Wc_2 = water content of second trial

- Plasticity Index (PI):

  $PI = LL – PL$

  If the liquid limit or plastic limits could not be determined, or the plastic limit is equal to or greater than the liquid limit, report the soil as non-plastic, NP.

12.0 Data Review

Refer to laboratory SOP BR-QA-019 for additional instruction on the requirements for data review. The following sections summarize the general procedure as described in the data review SOP.

12.1 Primary Review

Verify that the batch editor is complete and all observations have been recorded in the TALS Batch Worksheet. Review the results against acceptance criteria. If acceptance criteria are not met, perform corrective action or make arrangements for corrective action with another analyst.

Set results to primary or rejected as appropriate. Record all instances where acceptance criteria are not met with a nonconformance memo (NCM).

Verify project requirements or program specific requirements (PRS) specified for the job(s) included in the batch were followed and met. If not, immediately notify the project manager (PM) to determine an appropriate course of action. Record decisions made in the data review checklist.

Set the batch to 1st level review.

12.2 Secondary Review

Record the review using the data review checklist.

Review project requirements or program specific requirements (PRS) specified for the job(s) included in the batch and verify these requirements were followed and met. If not, consult with the primary analyst to determine cause. Any decisions made should be recorded on the data review checklist and retained as part of the analytical record.

Review the TALS batch editor to verify ancillary information for the work performed is filled in.

Verify that that the procedures in this SOP were followed. If a discrepancy between the SOP and the analytical record is found, consult with the primary analyst to determine the source of the discrepancy. Resolve the discrepancy and verify any modifications to the SOP are properly documented and were approved by laboratory management.

Spot-check ~15% of samples in the batch to verify data.

Verify acceptance criteria were met. If not, verity that corrective actions were performed and the nonconformance was documented with an NCM. Review the NCM to verify the form is filled out and the requisite information has been included in the internal comments tab. If corrective action was not performed and the failure not documented, consult with the primary analyst to determine the cause. Consult with the primary analyst and department management to determine what actions should be taken, then follow-through with the decision made.

Run and review the deliverable. Fix any problems found.

When review is complete set the method chain to lab complete. Forward any necessary paperwork to report/project management.

13.0 Method Performance

13.1 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

14.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste- Satellite Container: 5 Gallon Plastic Bucket.

16.0 References / Cross-References

- ASTM Standard D 4318-05 "Standard Test Methods for Liquid Limit, Plastic Limit and Plasticity Index of Soils". ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

17.0 Method Modifications

#	Method Reference	Modification	Technical Justification
1	ASTM Method D4318-05 Section 10.1	Method states to use the wet preparation procedure unless dry preparation is specified. The laboratory's practice is to use dry preparation for samples containing particles retained on the #40 sieve.	Both preparation methods are approved in the method.

18.0 Attachments

None

19.0 Revision History

BR-GT-011, Revision 8:
- Title Page: Updated approval signatures.
- All Sections: Replaced LIMS with TALS
- Added section 12.0, Data Review, and renumbered following sections accordingly.

BR-GT-011, Revision 7:
- Title Page: Updated approval signatures.
- Section 5.2: Updated MSDS to SDS
- Section 10.0: Updated calibration procedure
- Section 10.2.3: Addition of process to report results when the test is not amendable for the method
- Section 10.3: Addition of process to report results when the test is not amendable for the method
- Attachments: Removed Figure 1.

BR-GT-011, Revision 6:
- Title Page: Updated approval signatures.
- All Sections: changed DI water to reagent water.
- Section 1.0: Distinguished the difference when the laboratory will use wet or dry preparation.
- Section 2.0: Addition of dry preparation summary.
- Section 6.0: Added missing equipment
- Section 10.2: Changed procedure to reflect lab practice
- Section 16.0: Addition of modification table

Title: Water (Moisture) Content of Soil and Rock by Mass (ASTM D2216- 05, Method B)

Approval Signatures:

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Approval Date: March 27, 2018

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

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1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of water content of soil, rock, and similar materials where the reduction in mass by drying is attributed to loss of water.

The procedure is applicable to solid materials as the term is used to mean naturally occurring mineral particles of soil and that are not readily soluble in water. The procedure should not be used to determine water content in materials with substantial amounts of soluble solids or materials that contain extraneous matter or in marine sediments. For these types of materials, ASTM recommends special treatment or qualification of analytical results. ASTM methods for special treatment are listed in ASTM D2216-05 but are not currently offered by the laboratory. If laboratory analysis on such materials is desired, the laboratory recommends that procedures for treatment of samples and reporting specifications be specified by the customer prior to analysis.

2.0 Summary of Method

A portion of sample is dried in an oven maintained at a temperature of 110 ± 5 ºC for 16 hours or until constant mass. The loss of mass due to drying is considered to be water. The water content is calculated as the difference in the mass of the wet sample and the mass of the dry sample.

This SOP is based on the following reference method:

- ASTM Standard D 2216-05, 2005, "Determination of Water (Moisture) Content of Soil and Rock by Mass", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

If the laboratory's procedure has been modified from the reference method, a list of modifications will be provided in Section 16.0.

3.0 Definitions

- **Water Content by Mass:** The ratio of the mass of water contained in the pore spaces of soil or rock material, to the solid mass of particles in that materials, expressed as a percentage. A standard temperature of 110 ± 5℃ is used to determ ine these masses. (ASTM D2216-05)
- **Constant Mass:** The state that a water content specimen has attained when further heating causes or would cause less than 1% or 0.1% additional loss in mass. (ASTM D2216-05)

4.0 Interferences

This methods does not have defined interferences, however care should be taken when subsampling non-homogenous samples. Refer to SOP BR-QA-020 for subsampling techniques.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

There are no materials with a health rating of 3 or 4 used in this procedure. If a chemical material is listed, employees must review the information in the SDS (Safety Data Sheet) for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Drying Oven, capable of temperature measurements at 110°C (±5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum Pans, Fisher Scientific or equivalent.
- Stainless Steel Spatulas and Spoons, Fisher Scientific or equivalent.
- Heat shield gloves / Oven Tongs, Fisher Scientific or equivalent.

7.0 Reagents and Standards

Not Applicable

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. The reference method specifies that soil samples should be collected and preserved in accordance with ASTM D 4220 Section 8, Groups B, C or D for soils and rock samples collected in accordance with D 5079, Section 7.5.2.

Listed below are the laboratory recommended container types, sample amount, storage conditions and required holding times for analysis:

Matrix	Sample Container	Sample Amount	Storage	Holding Time
Solid	Glass	100-200 g	3-30℃	NA

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Calibration and Standardization

Check the calibration of the balance using at least 2 Class S weights that bracket the range of use and the temperature of the drying oven(s) on each day of use, prior to use. Record in the logbook designated for this purpose. Refer to SOP BR-QA-012 for support equipment calibration and checks.

10.2 Analysis

Use a sample amount that corresponds to the to the sieve size in the chart provided below.

Visually inspect the sample to identify the sieve size for which 100% of material will pass.

The reference method recommends the following sample amounts for analysis based on maximum particle size. If less than the recommended amount of sample was provided, use the amount of sample available and record the anomaly with a LIMS nonconformance memo (NCM).

Maximum Particle Size (mm)	Standard Sieve Size	Sample Mass for Analysis
2 or less	# 10	20 g
2 to 4.75	# 4	100 g
4.76 to 9.5	3/8 inch	500 g
9.6 to 19.0	3/4 inch	2.5 Kg
19.1 to 37.5	1 ½ inch	10 Kg
37.6 to 75.0	3 inch	50 Kg

Mix the sample thoroughly following the homogenization procedures specified in laboratory SOP BR-QA-020.

Label a clean aluminum pan with the sample ID then measure and record the weight of the pan to the nearest 0.01 g.

Weigh the pre-determined sample mass into the pan and record the combined weight of the pan and the wet sample. Repeat for each sample.

Check the temperature of the drying oven(s) to ensure that the oven is within 105-115℃; then place the pans in the drying oven. Dry the samples for 16 hours or until constant mass.

Remove the pans from the oven and allow the pans to cool to room temperature. Measure and record the weight of the pan and dried sample.

Calculate the moisture content using the equation given in Section 11.0.

NOTE: Analysis is not always performed using the recommended sample amounts specified in the reference method because smaller sample amounts are typically received by the laboratory. If additional volume is unavailable the lab will use the volume provided and create an NCM.

11.0 Calculations / Data Reduction

11.1 Calculation

Moisture Content

$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)] * 100$

Where:

w = water content, %

M_{cws} = mass of container and wet sample, g

M_{cs} = mass of container and oven dry sample, g

M_c = mass of container, g

11.2 Data Review

Review project documents, Project Plan (PP), Project Memo or any other document/process used to communicate project requirements from within LIMS to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

This section is not applicable to this procedure.

12.2 Demonstration of Capabilities (DOC)

Analyze Ottawa sand in quadruplicate as a demonstration of capability initially on learning the method, and annually thereafter. Use for form FQA048 as documentation of a successful DOC.

12.1 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices conducted are consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste- Satellite Container: 5 Gallon Plastic Bucket.

15.0 References / Cross-References

- ASTM Standard D 2216-05, 2005, "Determination of Water (Moisture) Content of Soil and Rock by Mass", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- TestAmerica Corporate Safety Manual, current version.
- Laboratory SOPs as referenced, current version.

16.0 Method Modifications

None

17.0 Attachments

None

18.0 Revision History

Revision 8.1

- Title Page: Updated Approval Signatures
- Section 4.0: added reference to subsampling SOP (BR-QA-020).
- Section 8.0: corrected storage temperature to match reference method.
- Section 10.1: added reference to BR-GT-012
- Section 11.2: replaced with most current verbiage for Data review of Geotechnical methods
- Section 12.0: added section regarding method performance.
- Section 18: removed older revision history and added statement of QA retention.
- Minor formatting update throughout

Previous revisions are retained by the QA department.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TOTAL SUSPENDED SOLIDS

(GL-GC-E-012 REVISION 15)

APPLICABLE TO METHODS:

Standard Methods 22nd Edition 2540 D-2011

PROPRIETARY INFORMATION

TABLE OF CONTENTS

1.0 STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS

2.0 METHOD CODE

2.1 Standard Methods 22nd Edition 2540 D-2011

3.0 METHOD OBJECTIVE/PURPOSE

This procedure is used to measure total suspended solids (TSS) in waters and wastewaters. TSS are those solids that are retained by a standard glass fiber filter and dried to a constant weight at 103 to 105 °C.

4.0 METHOD SUMMARY

4.1 Summary: In this gravimetric procedure, a water sample is filtered through a preweighed glass fiber filter. The filter is then dried to a constant weight at 103 to 105 °C. The weight of the residue on the filter represents the total suspended solids.

4.2 Synonym: Residue, total non-filterable

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid samples. In these cases the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is seven days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples may be stored in glass or plastic containers.

7.2 No preservatives are required. Preserved samples should not be analyzed.

7.3 Non-homogeneous particles such as leaves, sticks, fish, and lumps of fecal material should be excluded from the sample.

7.4 Refrigerate samples at 0 ≤ 6 °C until the start of analysis to minimize microbiological decomposition of solids.

8.0 INTERFERENCES/LIMITATIONS

8.1 Too much residue on the filter will entrap water and may require prolonged drying.

8.2 For samples that are high in dissolved solids, thoroughly wash the filter to ensure the removal of the dissolved material.

8.3 Prolonged filtration times resulting from filter clogging may produce high results due to the excessive capture of solids on the clogged filter.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 4 mg/L to 20,000 mg/L

9.2 Method detection limit (MDL): Refer to current MDL study.

9.3 Method precision: Refer to current SPC limits.

9.4 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 Desiccant: Material used to absorb moisture.

10.2 Gravimetric: Pertaining to measurement by weight.

10.3 Hygroscopic: Attracting, absorbing, and retaining atmospheric moisture.

10.4 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.5 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus

10.6 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.7 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.8 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

10.9 CRDL: Contract Required Detection Limit

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNING

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

13.3 All personnel performing this procedure are trained in and follow the procedures in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Sartorius Basic BA210S or comparable analytical balance capable of weighing to 0.0001 g

NOTE: The balance must be calibrated in accordance with the procedure outlined in GL-LB-E-002 for Balances.

15.2 VWR 1370FM or comparable drying oven for operation at 103 to 105 °C

NOTE: The oven's temperature is monitored in accordance with GL-LB-E-004.

15.3 Desiccator with a color indicating desiccant

15.4 Glass fiber filter paper, 4.7 cm

NOTE: If filters are not certified to be pre-washed they must be prepared according to step 19.2.

15.5 Filtration flask (minimum size: 1 L)

15.6 Magnetic filter funnel

15.7 Tweezers

15.8 Vacuum source

15.9 Disposable pipets

15.10 Thermometer verified according to GL-QS-E-007 for Thermometer Verification and capable of measuring temperatures of 103 to 105 °C.

15.11 Aluminum weigh boats

15.12 Volumetric flasks and/or beakers, various sizes

15.13 Stirring apparatus and stir bars

15.14 Graduated cylinders of various sizes

16.0 REAGENTS

16.1 ASTM Type I deionized (DI) water. (Refer to GL-LB-E-016)

16.2 Desiccant

16.3 Celite

17.0 PREPARATION OF SAMPLES

NOTE: It is recommended that if less than 250 mL is required, sample is stirred with a magnetic stirrer at a speed to shear larger particles to a more uniform particle size.

18.0 PREPARATION OF STANDARDS

18.1 500 mg/L Celite standard.

NOTE: This standard serves as the LCS.

18.2 Add 0.0500 g of Celite to a 100 mL volumetric flask that is partially filled with DI water.

18.3 Bring to volume with deionized water. Mix well.

18.4 Prepare a separate standard for each LCS and LCS duplicate.

18.5 Document preparation of standards in AlphaLIMS according to GL-LB-E-007 for Laboratory Standards Documentation and GL-GC-E-004 for General Chemistry Standards, Definitions, and Preparation.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 Preparation of desiccators:

19.1.1 Ensure that the desiccant is activated by observing the blue color indicator.

NOTE: If < 50% of the indicator desiccant is blue, change the desiccant.

19.1.2 Desiccator must be sealed. Any moisture absorbed by the filters can cause erroneous results.

19.2 Filter papers

NOTE: If pre-washed filter papers are being used, proceed to step 22.

19.2.1 Place a glass fiber filter in the filter apparatus.

19.2.2 Rinse with three successive portions of approximately 20 mL of DI water.

19.2.3 Apply vacuum until the water is removed from the filter.

19.2.4 Place the filter on aluminum foil in an oven to dry at 103 to 105 °C for at least one hour.

19.2.5 Remove the filter from the oven and cool it in a desiccator for approximately 30 minutes.

19.2.6 Weigh each filter and record its weight in the appropriately labeled column of AlphaLIMS.

19.2.7 Repeat the cycle of rinsing, drying, desiccating, and weighing until a constant weight is obtained for each filter.

19.2.8 Store the washed and dried filter in a desiccator.

19.2.9 Alternatively, pre-washed filters may be used as purchased.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 A matrix duplicate is analyzed for every batch of $\leq$ 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 A MB and LCS are analyzed for every batch containing ≤ 20 samples.

NOTE: An LCS duplicate is analyzed per client request.

20.2 Acceptance limits:

20.2.1 Matrix Relative Percent Difference (RPD): Refer to current SPC limits.

NOTE: If the difference between the sample concentration and duplicate concentration is less than or equal to the PQL and within a PQL value of each other, the results are acceptable even though the RPD may exceed current SPC limits.

20.2.2 Method blank: CRDL ≤ MB ≤ CRDL or ≤ ½ CRDL for any state of North Carolina samples.

20.2.3 LCS: Refer to current SPC limits.

20.2.4 LCS RPD: Refer to current SPC limits.

20.3 Handling out-of-control situations:

20.3.1 Notify the Group Leader immediately.

20.3.2 If the matrix or LCS RPD, MB, and/or LCS recovery fall outside of current acceptance limits, the samples to which the unacceptable quality control (QC) pertains must be reanalyzed.

20.3.3 Document in the case narrative the specific QC that is out of control and cross-reference data from any subsequent reanalysis.

20.3.4 If filtering times are greater than 10 minutes, use less sample aliquot.

21.0 RUN SEQUENCE

21.1 MB

21.2 LCS

21.3 Samples 1 through *x* where $x \leq 10$

21.4 Sample Duplicate

21.5 Repeat 21.3 through 21.4 for every 10 samples in the batch.

22.0 PROCEDURE

22.1 Calibration of equipment/instrumentation:

22.1.1 Balance

Ensure that the analytical balance to be used has been calibrated and it is within control limits before use. Refer to the balance logbook and GL-LB-E-002 for Balances.

22.1.2 Oven

22.1.2.1 Make sure that the oven to be used is at a temperature that is within acceptance limits.

22.1.2.2 Control limits for the drying oven are documented on the temperature log.

22.1.2.3 The oven temperature log format provides the required documentation to ensure that the oven temperature was in control during the drying process.

22.1.2.4 Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators and Other Similar Devices.

22.2 Analysis:

22.2.1 Label an appropriate number of aluminum weigh boats (one per sample and for each QC sample).

22.2.2 Remove, immediately prior to weighing, the pre-washed glass fiber filter, prepared as described in section 19.0, from the desiccator.

NOTE: **NEVER** touch the filter with your hands. Always use tweezers or tongs.

22.2.3 Record the weigh boat ID, sample number, and the weight of each filter to be used in the appropriate columns in the data entry screen in AlphaLIMS.

22.2.4 Dry the filters for at least one hour at 103 to 105 °C.

22.2.5 Remove the filters from the oven and cool in a desiccator until they reach room temperature. This takes approximately 30 minutes.

22.2.6 Weigh each filter and record its weight a second time in the appropriately labeled column of AlphaLIMS.

22.2.7 Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained for each filter. Constant weight is defined as a weight loss or gain of ≤ 0.5 mg or 0.0005 g.

22.2.8 Place the filter on the filter apparatus and wet with a small amount of reagent grade water, to seat the filter.

22.2.8.1 If aliquots greater than 250 mL are to be used, shake container and rapidly transfer the sample to the filter by means of a graduated cylinder

NOTE: It is recommended that for volumes less than 250 mL, thoroughly shake the sample to be analyzed. Add a magnetic stir bar and stir at a speed to shear larger particles, to obtain a more uniform particle size.

22.2.8.2 While stirring, pipet a measured volume onto the seated filter, pipeting from the approximated midpoint of the container, but not in the vortex.

22.2.9 Record the volume of sample used in AlphaLIMS.

NOTE: The volume of sample to be used can be increased or decreased depending upon the matrix of the sample. If there is minimal residue (< 1.0 mg) on the filter after filtering 100 mL, additional 100 mL aliquots of the sample must be filtered. In some cases the filter may clog, preventing additional sample from being filtered. The analyst may use less than 1000 mL of sample if the filtration time takes ≥ 10 minutes.

NOTE: 500 mL of DI water must be filtered for the MB.

22.2.10 Apply the vacuum and filter the sample.

22.2.11 Rinse the graduated cylinder three times with DI water and transfer the rinsate to the funnel to ensure that all residue is transferred.

22.2.12 Remove any lingering residue from the funnel by rinsing thoroughly with three successive volumes of DI water (approximately 10 mL each).

22.2.13 Continue to apply the suction after the filtration is complete in order to remove as much water as possible.

22.2.14 Carefully remove the filter from the filter apparatus.

22.2.15 Place the filter back in its aluminum weigh boat.

22.2.16 Repeat steps 22.2.8 through 22.2.15 for each sample or QC sample in the batch.

22.2.17 Dry the filters for at least one hour at 103 to 105 °C.

NOTE: The amount of residue on the filter should fall in the range of 10 to 200 mg.

22.3 Calculation/reporting of results:

22.3.1 Calculate TSS as follows:

$$\text{TSS (mg/L)} = \frac{A - B \times 1{,}000}{C}$$

Where:

A = Final weight of the filter plus residue in g

B = Weight of the filter paper in g (This is the last weight of the filter obtained prior to filtration.)

C = Volume of the sample in (L)

22.3.2 Results are reported in mg/L.

22.3.3 RPDs are calculated as follows:

$$\frac{([\text{TSS mg/L}]\text{sample} - [\text{TSS mg/L}]\text{duplicate})}{\text{Average}[\text{TSS mg/L}]\text{of sample and duplicate}} \text{X } 100$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

25.0 DATA TRANSMITTAL

When a batch is issued a status of DONE, the data are automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 Ovens and Thermometers

Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices.

27.2 Balances

Refer to GL-LB-E-002 for Balances.

27.3 Procedure for the maintenance of desiccant

27.3.1 Analysts are responsible for ensuring that the desiccators are maintained by replacing the desiccant whenever 50% of the blue indicator starts to turn pink.

27.3.2 Dry desiccant for reuse as follows

27.3.2.1 Spread desiccant out in an aluminum pan.

27.3.2.2 Place in drying oven capable of maintaining 105 °C for one hour or more.

27.3.2.3 Remove from the oven.

NOTE: All desiccants should be blue.

27.3.2.4 Place in a desiccator immediately to cool.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VARIATION AND VERIFICATION

29.1 Step 19.2.2 differs from SM 2540 D-2011. Both methods mention three 20 mL rinses of the filter paper with deionized water during filter preparation. As written, this SOP asks for the filter papers to be rinsed only once with 100 mL of DI water.

29.2 Constant weight is defined in SM 2540 D-2011 as a weight loss or gain of < 4% of the previous weight or 0.0005 g. Constant weight is defined in this SOP as a difference equal to or less than 0.0005 g.

29.3 MDLs are calculated in accordance with GL-LB-E-001 for Determination of Method Detection Limits.

29.4 Step 22.2.8 differs from SM 2540 D-2011, which calls for the pipetting of the sample aliquot to the filter instead of transferring by a graduated cylinder.

30.0 REFERENCES

30.1 Federal Register 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act," April 4, 1995.

30.2 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, Method 2540 D-2011.

30.3 Compilation of ASTM Standard Definitions. Sponsored by ASTM Committee on Terminology, 7th Edition, Philadelphia, American Society for Testing and Materials, 1990.

30.4 Manual of Methods for Chemical Analysis of Water and Wastes. EPA Technology Transfer, EPA-625/6-74-003a, 1976.

31.0 HISTORY

Revision 15: TSS calculation revised.

Revision 14: Revised to include model of analytical balance and drying oven being used to comply with SCDHEC audit finding.

Revision 13: Revised quality control requirements for method blank for state of North Carolina samples.

Revision 12: Updated Standard Methods reference for MURII compliance.

Revision 11: Replace Type II with Type I Deionized water.

Revision 10: Added a definition, a SOP reference, and a procedural step.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR TOTAL, TOTAL INORGANIC, AND TOTAL ORGANIC CARBON (TOC)

(GL-GC-E-093 REVISION 16)

APPLICABLE TO METHODS:
EPA Method 415.1
EPA SW-846 Methods 9060/9060A
Standard Methods 22nd Edition, SM 5310 B-2011

PROPRIETARY INFORMATION

GEL

GEL'S
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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL, TOTAL INORGANIC, AND TOTAL ORGANIC CARBON (TOC)

2.0 METHOD CODE

2.1 EPA Method 415.1

2.2 EPA SW-846 Method 9060/9060A

2.3 Standard Methods 22nd Edition, SM 5310 B-2011

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the procedure used to run samples for total, total inorganic, and total organic carbon using the OI Analytical Model 1030W Aurora TOC analyzer.

4.0 METHOD SUMMARY

4.1 Total organic carbon is converted to carbon dioxide by chemical oxidation of the organic carbon in the sample. The carbon dioxide is measured using a non-dispersive infrared detector.

4.2 Synonym: Non-purgeable organic carbon

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. If the sample is very viscous or heavily particulated, the sample is treated as a solid and SOP GL-GC-E-062 is used.

NOTE: SC DHEC requires analysis by SW-846 9060/9060A if samples are not drinking water or wastewater and the data are to be used for regulatory purposes.

6.0 HOLDING TIME

Holding time is 28 days from the time and date of collection until the start of analysis unless otherwise specified.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Storage of samples in amber glass bottles is preferred. Polyethylene bottles may be used if blanks are collected to show that the containers do not contaminate the samples.

7.2 Unless samples are to be analyzed within 15 minutes of collection, they should be acidified to a pH of less than 2 with sulfuric acid, phosphoric acid or hydrochloric acid.

7.3 Samples should be stored at $0° \leq 6°$ C.

7.4 If the concentration of dissolved organic carbon is to be determined, samples should be filtered through a 0.45 µm filter at the time of collection.

8.0 INTERFERENCES

Carbonates and bicarbonates must be removed before analysis for TOC. The sparging of liquid samples removes carbonate and bicarbonate interferants.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.00 to 20 mg/L with the sample loop set at 5 mL loop size.

9.2 Calibration range: 1 to 20 mg/L.

9.3 Method detection limit (MDL): Refer to current MDL study.

9.4 Method precision: < or equal to 20% RPD.

9.5 Method accuracy: 85%-115%.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL.

10.2 Laboratory Control Sample (LCS): A standard, usually of the same matrix as the sample batch being organized, taken through the same prep process as the samples then analyzed with the batch.

10.3 Total Organic Carbon: All carbon in a sample besides carbonates and bicarbonates.

10.4 Non-purgeable Organic Carbon: All organic carbon that is not removed by sparging.

10.5 Total Carbon: Total amount of carbon in a sample.

10.6 Total Inorganic Carbon: All inorganic carbon in a sample that is separated from organic carbon by acidification.

10.7 Dissolved Organic Carbon: All organic carbon in a sample that has been filtered through a 0.45 micron filter.

10.8 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, computer printouts of the data are generated. These dated hard copies of the data are stored in the TOC 1030W binder. Results are uploaded into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 IO Analytical Model 1030W Aurora TOC Analyzer including:

15.1.1 Reaction module

15.1.2 Detector/electronics module

15.1.3 Printer module

15.1.4 Autosampler module

15.2 Compressed nitrogen (zero grade) and two stage regulator

15.3 Flow meter

15.4 Personal computer (for entering data)

16.0 REAGENTS

16.1 Raw materials: (Chemicals should be at least ACS grade or equivalent)

16.1.1 Potassium acid phthalate, $KHC_8H_4O_4$

16.1.2 Concentrated phosphoric acid, H_3PO_4 (85%)

16.1.3 5% (by volume) Phosphoric acid reagent: Carefully add 59 mL concentrated phosphoric acid to 500 mL DI water, and dilute to 1 L.

16.1.4 ASTM Type I deionized water (see GL-LB-E-016)

16.1.5 Sodium bicarbonate, $NaHCO_3$

16.2 Persulfate reagent:

16.2.1 Dissolve 100 g sodium persulfate in a 1 liter volumetric flask using deionized (DI) water.

16.2.2 Bring to volume with DI water.

17.0 PREPARATION OF SAMPLES

Not applicable.

18.0 PREPARATION OF STANDARDS

Potassium Phthalate (also known as potassium hydrogen phthalate) is used for the preparation of standards. The standard is valid for one year from opened date or manufacturer's expiration date, whichever is shortest.

18.1 TIC Standard Solution (2000mg/L)

18.1.1 Weigh 14 g of Sodium Bicarbonate and dilute to 500 mL of DI water in a volumetric flask. This yields a 2000 mg/L solution which expires in 6

months. This solution should be purchased from a certified vendor, if available.

18.2 Primary TOC Standard Solution (2000 mg/L)

18.2.1 Weigh 0.850 g of potassium acid phthalate and dilute to 200 mL volume with DI water in a 200 mL volumetric flask. This yields a 2000 mg/L solution. Standard expires six months from preparation date. This solution should be purchased from a certified vendor, if available.

18.3 TIC/TOC Working Standard (20 mg/L)

18.3.1 Transfer 2.5 mL of the primary TIC/TOC stock standard solution to the 250 mL volumetric flask and dilute to 250 mL with DI water.

18.4 TIC/TOC Working Standard (10 mg/L)

18.4.1 Transfer 2.5 mL of the primary TIC/TOC stock standard solution using 500 mL volumetric flask and dilute to 500 mL with DI water.

18.5 TIC/TOC Working Standard (1 mg/L)

18.5.1 Transfer 0.125 mL of the primary TIC/TOC standard solution to the 250 mL volumetric flask and dilute to 250 mL with DI water.

18.6 TOC Working Standard (5 mg/L)

18.6.1 Transfer 0.625 mL of the TIC/TOC to the partially filled flask. Dilute to 250 mL with DI water.

NOTE: Working standards expire 1 week after preparation.

18.7 Secondary TIC/TIC Stock Standard

18.7.1 Using a different lot number of Sodium Bicarbonate, weigh 14 g of Sodium Bicarbonate a dilute to 500 mL with DI water in a volumetric flask. This yields a 2000 mg/L solution which expire after 6 months. This solution should be purchased from a certified vendor, if available.

18.8 Secondary TOC Stock Standard

18.8.1 Using a different lot of potassium phthalate, weigh 0.850 g of potassium acid phthalate and dilute to 200 mL volume with DI water in a 200 mL volumetric flask. This yields a 2000 mg/L solution. Standard expires six months from preparation date. This solution should be purchased from a certified vendor, if available.

18.9 10 mg/L Working LCS/ICV/CCV

18.9.1 Transfer 2.5 mL of the secondary TIC/TOC stock standard to the 500 mL volumetric flask and dilute to 500 mL with DI water. This solution expires one week from preparation.

19.0 PREPARATION OF STANDARDS AND QUALITY CONTROL SAMPLES

19.1 Documentation of standards and their preparation are maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

19.2 Laboratory Control Sample (LCS): (See 18.9)

19.3 Calibration standards: The concentrations used are listed below:

19.3.1 0.0 mg/L

19.3.2 1 mg/L

19.3.3 5 mg/L

19.3.4 10 mg/L

19.3.5 20 mg/L

19.3.6 Calibration standards are made up using primary source stock standard.

19.4 Initial Calibration Verification (ICV): The ICV is a 10.0 mg/L standard made from the second source stock standard. The ICV must be analyzed immediately after the calibration standards and analyzed at the start of each analytical week. The ICV standards are made up on a weekly basis. (See 18.9)

19.5 Continuing Calibration Verification (CCV): The CCV is a 10.0 mg/L standard made from the second source stock standard. A CCV must be run after every 10 samples and after the last sample in the run. The CCV standards are made up on a weekly basis. (See 18.9)

20.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

20.1 Refer to Chapter 4: Operation of the OI Model 1030W Aurora TOC Analyzer Operator's Manual.

20.2 Before a run is started, make sure there is an adequate amount of sodium persulfate reagent to complete the analysis. Also make sure the 5% phosphoric acid solution and DI H_2O containers are full.

20.3 Prior to the start of analysis, ensure that the nitrogen flow is between 40 and 60 psi.

21.0 QUALITY CONTROL (QC) REQUIREMENTS

21.1 Instrument QC

21.1.1 An initial calibration verification (ICV) is analyzed immediately after the calibration standards and at the start of each analytical week. This standard must be made from a different source than the calibration standards.

21.1.2 An initial calibration blank (ICB) is analyzed following the ICV.

21.1.3 A continuing calibration verification (CCV) is analyzed after every 10 analytical samples and after the last analytical sample in the run.

21.1.4 A continuing calibration blank (CCB) is analyzed after every CCV.

21.2 Batch QC

21.2.1 A matrix spike and a matrix duplicate are analyzed for every batch of $\leq$ 10 samples and for each set of ten samples in batches with > 10 samples (unless otherwise required by client contract).

21.2.2 A method blank and laboratory control sample (LCS) are analyzed at least once for every batch of 20 samples or less.

21.2.3 For liquid samples, the LCS is normally a 10 mg/L standard taken through the same process as the samples.

21.2.4 LCS duplicates are analyzed if required by client contract.

21.3 Acceptance limits:

21.3.1 Correlation coefficient must be 0.995 or greater.

21.3.2 ICV recovery must be 90-110% for all batches (unless otherwise specified by client contract). If not, the ICV should be remade and reanalyzed. If the ICV continues to be out of range, a re-calibration is then required.

21.3.3 CCV recovery must be 90-110% for all batches (unless otherwise specified by client contract). Any samples bracketed by a failing CCV must be reanalyzed with passing bracketing CCVs. If the CCV continues to be out of range, the instrument must be recalibrated.

21.3.4 Matrix relative percent difference (RPD): < or equal to 20% of RPD.

21.3.5 Matrix spike recovery: 85% -115%.

21.3.6 Method blank: Must be less than the CRDL.

21.3.7 LCS: refer to current SPC limits which are static for Drinking Water samples.

21.3.8 LCS RPD: refer to current SPC limits which are static for Drinking Water samples.

21.3.9 If analysis by EPA Method 415.1 is requested, the samples are analyzed in duplicate. The relative percent difference (RPD) between the two values must be ≤ 20% when the values are greater than 5 mg/L.

21.3.10 If analysis by SW-846 9060/9060A is requested, samples are analyzed in quadruplicate. The relative percent difference (RPD) between the values must be ≤ 20% when the values are greater than 5 mg/L.

21.4 Handling out-of-control situations:

21.4.1 If a sample result exceeds the concentration of the highest calibration standard, the sample must be diluted appropriately with DI water and reanalyzed.

21.4.2 The correlation coefficient must be at least 0.995. If it is less than 0.995 the calibration standards must be reanalyzed. Analysis of samples cannot begin until a correlation coefficient of 0.995 is obtained.

22.0 RUN SEQUENCE

22.1 Calibration standards, including DI water blank

22.2 ICV

22.3 ICB

22.4 Up to 10 analytical samples including LCS, method blank, and sample QC (refer to Section 20)

22.5 CCV (Continuing Calibration Verification)

22.6 CCB

22.7 Repeat steps 21.5 through 21.7 for remaining samples in the run ending with CCV and CCB.

23.0 PROCEDURE

23.1 Analysis: Refer to Chapter 4 (pages. 62 through 71), Operation of the Model 1030W Aurora Analyzer Operator's Manual.

23.2 Calculation/reporting of results:

23.2.1 As the data are obtained, they are uploaded into AlphaLIMS.

23.2.2 If a sample is analyzed by EPA 415.1, the average of the two replicates is reported for the TOC or Total Carbon Concentration.

23.2.3 For samples analyzed by SW 846-9060/9060A, all four replicates plus the average are reported for the TOC concentration.

24.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

Refer to OI Analytical Model 1030W Aurora TOC analyzer.

25.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

26.0 DATA TRANSMITTAL

When a batch is issued "DONE" status, it is made available to reporting personnel.

27.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

28.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to Chapter 4, page 74, Operation of the Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

29.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

30.0 METHOD VERIFICATION

30.1 To ensure accuracy, % error is calculated for the duplicate values of all concentrations greater than 1 mg/L.

30.2 The % error must be 10% or less for samples logged according to Method 415.1. If not, the samples must be reanalyzed.

31.0 REFERENCES

31.1 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, "Organic Carbon, Total," Method 415.1 (Combustion or Oxidation), March 1979.

31.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1C, SW-846, Third Edition, November 1986. Method 9060, "Total Organic Carbon," Revision 0, September 1996. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

31.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1C, SW-846, Third Edition, November 1986. Method 9060A,

"Total Organic Carbon," Revision 1, August 2002. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

31.4 OI Analytical Model 1030W Aurora Analyzer Operator's Manual.

31.5 Standard Methods 22nd Edition, SM 5310 B-2011. High-Temperature Combustion Method.

31.6 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3, July, 2019.

32.0 HISTORY

Revision 12: Preparation of Standards section added.

Revision 13: Updated procedure to include new instrument information and remove reference to old instrument. Updated the process of working standards.

Revision 14: Further method and procedure clarifications and updated to new instrument.

Revision 15: Updated the method concentration range from 0.2 to 0.00. Added reference to QAP in definitions. Added current DOD/DOE QSM version 5.1 and version 3.1, January 2017.

Revision 16: Updated sample preservation. Updated DoD QSM reference to Version 5.3, July 2019. Clarify acceptance limits for Drinking Water.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR

THE EXTRACTION AND ANALYSIS OF PER- AND POLYFLUOROALKYL (PFAS) SUBSTANCES USING LCMSMS

(GL-OA-E-076 REVISION 7)

APPLICABLE TO METHOD:
EPA Method 537.1 and 537.1 Modified
ASTM D7968-17A
Compliant with Table B-15, DOD QSM, Version 5.3 Requirements

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) USING SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/ TANDEM MASS SPECTROMETRY (LCMSMS)

2.0 METHOD REFERENCE

2.1. ASTM D7968-17A

2.2. EPA 537.1 Version 1.0

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) covers the determination of Per- and Polyfluoroalkyl substances (PFAS) in a wide variety of liquid matrices according to USEPA method 537.1 and other analytical protocols such as Department of Defense (DOD) and Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental laboratories.

4.0 METHOD SCOPE AND APPLICABLE MATRIX

4.1. Refer to Table I for compound list of PFAS by LCMSMS.

4.2. This method applies to the following matrices:

- 4.2.1. Groundwater
- 4.2.2. Drinking Water
- 4.2.3. Wastewater
- 4.2.4. Soil
- 4.2.5. Tissue

5.0 DISCUSSION

A 250-mL water sample is fortified with extraction internal standards or surrogates (drinking water) and passed through a solid phase extraction (SPE) cartridge to extract the method analytes and their corresponding isotopes. The compounds are eluted from the cartridge with 0.1% ammonia/methanol followed by a small amount of methanol. The extract is concentrated to 4 mL with nitrogen in a heated water bath, and then adjusted to a final volume of 5-mL in 80:20 (vol/vol) methanol: water. (96:4 vol/vol MeOH: water for drinking water).

A 2-gram soil is transferred to a 50 mL tube and fortified extraction internal standards. 5 mL of 0.1% ammonia/Methanol is added to each container. The sample is then shaken on a wrist action shaker for 30 minutes under basic conditions (pH ~ 9-10). The sample is then decanted and the process repeated twice more with 2.5 mL aliquots of 0.1% ammonia/Methanol. The extract is then centrifuged and a portion of the sample passed through an Envicarb SPE cartridge to remove interferences. The sample is then

concentrated to 4 mL on an N-EVAP. Add 1 mL of water to each extract. The sample is now ready for analysis.

A 2-gram tissue sample is transferred to a 50 mL tube and fortified extraction internal standards. 10 mL of 0.1% Ammonia/Methanol is added to each container. The sample is then shaken on a wrist action shaker for 30 minutes under basic conditions (pH ~ 9-10). The sample is then decanted and the process repeated twice more with 5 mL aliquots of 0.1% Ammonia/Methanol. The extract is then centrifuged and a portion of the sample passed through an Envicarb SPE cartridge to remove interferences. The sample is then concentrated to 4 mL on an N-EVAP. Add 1 mL of water to each extract. The sample is now ready for analysis.

A 25-µL injection is made into an LC equipped with a C18 column that is interfaced to an MS/MS. The analytes are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard technique. Extraction internal standards or surrogates (drinking water) are added to all Field and QC Samples to monitor the extraction efficiency of the method analytes. Injection internal standards are added to all samples, QC, standards and blanks prior to analysis to monitor matrix interference and instrument efficiency.

6.0 DEFINITIONS

6.1. Analysis Batch: A set of samples that is analyzed on the same instrument during a 24-hour period, including no more than 20 Field Samples, that begins and ends with the analysis of appropriate Continuing Calibration Verification (CCV) standards. Additional CCVs may be required depending on the length of the analysis batch and/or the number of Field Samples.

6.2. Calibration Standard (CAL): A solution prepared from the primary dilution standard solution and/or stock standard solution, extraction internal standard(s), and the injection internal standard(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6.3. Continuing Calibration Check (CCC): This standard will be referred to as a Continuing Calibration Verification (CCV) standard for this SOP. A CCV contains the method analytes, extraction internal standard(s) and injection internal standard(s). The CCV is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

6.4. Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination of precision,

and accurate quantitation is not expected at this level. Typically, the MDL is two to three times less than the lowest concentration used to calibrate the instrument.

6.5. Extraction Batch: A set of up to 20 Field Samples (not including QC samples) extracted together by the same person(s) during a work day using the same lot of SPE devices, solvents, surrogate, internal standard and fortifying solutions. Required QC samples include Laboratory Reagent Blank, Laboratory Fortified Blank, Laboratory Fortified Sample Matrix, and either a Field Duplicate or Laboratory Fortified Sample Matrix Duplicate.

6.6. Field Duplicated (FD1 and FD2): Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

6.7. Field Reagent Blank (FRB): An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

6.8. Laboratory Fortified Blank (LFB): Will be referenced as Laboratory Control Sample (LCS) in this SOP. A volume of reagent water or other blank matrix to which known quantities of the method analytes and all the preservation compounds are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

6.9. Laboratory Fortified Sample Matrix (LFSM): Will be referenced as a Matrix Spike (MS) in this SOP. A field sample to which known quantities of the method analytes are added in the laboratory. The MS is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate sample extraction and the measured values in the MS corrected for background concentrations.

6.10. Laboratory Fortified Sample Matrix Duplicate (LFSMD): Will be referenced as a Matrix Spike Duplicate (MSD). A duplicate of the Field Sample used to prepare the MS. The MSD is fortified, extracted, and analyzed identically to the MS. The MSD is used instead of the Field Duplicate to assess method precision when the occurrence of method analytes is low.

6.11. Matrix Duplicate (MD): Will be referenced as a Sample Duplicate (DUP). This is a duplicate of the Field Sample. It is extracted and analyzed identically to the

sample. The DUP is used to assess method precision when the occurrence of method analytes is low.

6.12. Laboratory Reagent Blank (LRB): Will be referenced as the Method Blank (MB) in this SOP. An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents, sample preservatives, extraction internal standards, and injection internal standards that are used in the analysis batch. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

6.13. Lowest Concentration Minimum Reporting Level (LCMDL): The single laboratory LCMRL is the lowest true concentration for which a future recovery is expected, with 99% confidence, to be between 50 and 150% recovery.

6.14. Minimum Reporting Level (MRL): The minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. The defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte and can only be used if acceptable QC criteria for this standard are met. A procedure for verifying a laboratory's MRL is provided in Appendix 5. This is also referenced as the LOQ. Typical MRLs for this method 2 ng/L for waters and 500 ng/Kg for solids.

6.15. Quality Control Sample (QCS): Will be referenced as the Initial Calibration Verification (ICV) in this SOP. A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. The ICV is analyzed directly after the calibration curve and is used to check calibration standard integrity. If an alternate source is not available, a different lot from the same source may be used.

6.16. Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined level confidence to be statistically different from a blank. The LOD verification is typically spiked at two times the MDL.

6.17. Limit of Quantitation (LOQ): The lowest concentration level of the initial calibration curve used to quantitate an analyte. The LOQ verification is typically spiked at the PQL. This is also referenced as the MRL (for drinking water only).

6.18. Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

6.19. Surrogate Standard – A standard added prior to sample extraction used to monitor unusual matrix effects, sample processing errors, and extraction efficiency. These are used for drinking water analysis only. They are: $^{13}C_4$-PFOS, $^{13}C_3$-PFBA, $^{13}C_2$-PFOA, and $^{13}C_2$-PFDA. These surrogates are added at a concentration of 250 ng/L. Surrogates are added to each blank, laboratory control sample (LCS), matrix spike (MS), matrix spike duplicate (MSD) and sample prior to the extraction.

6.20. Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

7.0 INTERFERENCES

7.1. All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by a reagent water rinse. Non-volumetric glassware can be heated in a muffle furnace at 400 °C for 2 h or solvent rinsed. Volumetric glassware should be solvent rinsed and not be heated in an oven above 120 °C. Store clean glassware inverted or capped. Do not cover with aluminum foil because PFASs can be potentially transferred from the aluminum foil to the glassware.

NOTE: PFAS standards, extracts and water samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAS analytes, ES and IS standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in HDPE containers.

7.2. Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. The method analytes in this method can also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc. All items such as these must be routinely demonstrated to be free from interferences (less than 1/3 the MRL for each method analyte) under the conditions of the analysis by analyzing laboratory reagent. **Subtracting blank values from sample results is not permitted**.

7.3. 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 water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent. Total organic carbon (TOC) is a good indicator of humic content of the sample.

7.4. Relatively large quantities of the preservative are added to sample bottles for drinking water samples. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks particularly when new lots of reagents are acquired.

7.5. SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the

presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

8.0 SAFETY, HEALTH, ENVIRONMENTAL HAZARDS AND POLLUTION PREVENTION

8.1. Wear eye protection with side shields while working in the laboratory.

8.2. All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

8.3. Personal protective equipment

8.3.1. Gloves are required when working with solvents, standards and samples. Solvents, along with any solute in them, can absorb easily through the skin.

8.3.2. Work under a hood when using concentrated acids.

8.3.3. To protect clothes and skin from corrosive material, wear a lab coat.

8.4. Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines to follow:

8.4.1. To monitor radioactive exposure, wear a dosimeter at all times while working in the lab.

8.4.2. Wear a plastic apron over lab coat when working with radioactive samples.

8.4.3. Protect counter tops with counter paper or work from radioactive sample handling trays.

8.4.4. Prohibit admittance to immediate work area.

8.4.5. Post signs indicating radioactive samples are in the area.

8.4.6. Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

8.4.7. Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.5. All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5.1. Segregate solid wastes from liquid wastes in the satellite area containers.

8.5.2. Segregate oil wastes from water-soluble wastes in the satellite area containers.

8.6. In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

8.7. Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

8.8. Refer to SOP GL-LB-N-001 Safety, Health and Chemical Hygiene Plan for additional general safety and health information pertaining to the laboratory.

9.0 APPARATUS AND MATERIALS

9.1. Labware

9.1.1. Polypropylene Conical Tubes – 15 mL and 50 mL

9.1.2. pH paper – pH range 1-14

9.1.3. Vials: 4 mL narrow- mouth HPDE bottles with plastic caps for standards storage.

9.1.4. Autosampler Vials – Polypropylene 0.3-mL autosampler vials with polypropylene caps.

9.1.5. Graduated Cylinders – appropriate sizes

9.1.6. Eppendorf Pipet and tips

9.2. Top loading balance

9.3. Vortex mixer

9.4. Wrist Action Shaker

9.5. Solid Phase Extraction (SPE) apparatus for using cartridges.

9.5.1. SPE Cartridges – Strata™ XL-AW 100 µm Polymeric Weak Anion

9.5.2. SPE Cartridges - Strata XL 100 um Polymeric Reverse Phase

9.5.3. SupelClean™ ENVI-Carb™ SPE Cartridge - (0.25g) 6 mL

9.5.4. Vacuum Extraction Manifold – A manual vacuum manifold with large volume sampler for cartridge extractions.

9.5.5. Sample Delivery System – Use of a polypropylene transfer tube system, which transfers the sample directly from the sample container to the SPE cartridge.

9.6. Liquid Chromatography (LC)/Tandem Mass Spectrometer (MS/MS) With Data System

9.6.1. Liquid Chromatography/Mass Spectrometry/Mass Spectrometry System - An analytical system complete with a binary gradient, programmable high-pressure liquid chromatograph, and a column heater capable of maintaining a temperature of 40° ± 1° C. The liquid chromatography

unit must be capable of accurate and repeatable flow rates of 0.2 mL/min to 1.0 mL/min. The mass spectrometer system must possess an electrospray ionization (ESI) interface capable of operating at flow rates stated above. The mass spectrometer system must be capable of negative ion analysis and consist of three quadrupoles for daughter fragmentation.

9.6.2. Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any LC/MS/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specific time or scan-number limits.

9.6.3. Analytical Column – Gemini 3 µm C18 110 Å LC column 50 x 2 mm.

9.6.4. Delay Column - Luna® 5 µm C18 (2) 100 Å 30 x 3 mm

10.0 REAGENTS AND STANDARDS

10.1. Source standards are purchased directly from certified vendors and may be diluted to make stock, intermediate, and/or working standards. Source standards expire per the vendor expiration date. Please refer to GL-LB-E-007 for further information regarding standards, their preparation, and control.

10.2. Calibration Standards: Calibration standards are prepared from intermediates of certified source standards. Calibration standards expire per the source standard vendor expiration date, or after one year from the open date, whichever is shorter. The calibration standards should be monitored for signs of degradation, and replaced as necessary.

10.3. Second-Source Calibration Standards: A standard purchased from a different certified vendor than the calibration standards or a different lot number from the same vendor as the calibration standards. These standards expire per the vendor's expiration date.

10.4. Laboratory Control Sample (LCS) and Matrix Spike (MS) Standards: The LCS and MS standards contain all of the compounds of interest. LCS and MS standards may be purchased pre-mixed as source standards, or may be prepared in the laboratory from certified source standards. All LCS and MS standards expire per the source standard vendor expiration date, or after one year from the open date, whichever is shorter.

10.5. Extracted Internal Standard (ES): The standard added to all samples and QC prior to extraction to monitor the efficiency of the extraction procedure. The ES

standard is prepared as an intermediate source standard and expires per the source standard vendor expiration date, or after one year from the open date of the source, whichever is shorter. This is used as the internal standard for drinking water samples.

10.6. Injected Internal Standard (IS) Solution: Internal standard is added to all samples, QC, and working standards prior to analysis. The IS standard solution is prepared as an intermediate source standard and expires per the source standard vendor expiration date, or after one year from the open date, whichever is shorter. This is used as the surrogate standard for drinking water samples.

10.7. Polypropylene Glycol Tuning Solution (PPG): A positive and negative PPG standard.

10.8. Nitrogen Gas, 99+%

10.9. Reagent water: Purified and does not contain interfering compounds or measurable quantities greater than 1/2 LOQ (1/3 LOQ for drinking water) of each method analyte of interest. (See Appendix 6 for all drinking water criteria). Prior to daily use, at least 3 L of reagent water should be flushed from the purification system to rinse out any build-up of analytes in the system's tubing. Water can also be purchased from a certified vendor.

10.10. White Quartz Sand -50+70 mesh.

10.11. Methanol - High purity, demonstrated to be free of analytes and interferences.

10.12. AMMONIUM ACETATE ($NH_4C_2H_3O_2$, CAS#: 631-61-8) – 97 % mass fraction or greater, demonstrated to be free of analytes and interferences.

10.13. 20 mM AMMONIUM ACETATE/REAGENT WATER – To prepare 1 L, add 1.54 g ammonium acetate to 1 L of reagent water. This solution is prone to volatility losses and should be replaced at least every 48 hours.

10.14. TRIZMA® PRESET CRYSTALS, pH 7.0 (Sigma cat# T-7193 or equivalent) – Reagent grade. A premixed blend of Tris [Tris(hydroxymethyl)aminomethane] and Tris HCL [Tris(hydroxymethyl)aminomethane hydrochloride]. Alternatively, a mix of the two components with a weight ratio of 15.5/1 Tris HCL/Tris may be used. These blends are targeted to produce a pH near 7.0 at 25 °C in reagent water. Trizma® functions as a buffer, and removes free chlorine in chlorinated finished waters. This will be added to drinking water samples only.

10.15. Acetic acid (CH_3COOH) – 99.9 % mass fraction.

10.16. Ammonium Hydroxide - ~25 % mass fraction.

10.17. Acetate Buffer 0.025 mol/l, pH 4. - Mix 0.5 mL of acetic acid (10.15) with 349.5 ml of water (10.9). Dissolve 0.116 g of ammonium acetate (10.11) in 60 mL of water (10.9). Mix 200 ml of the diluted acetic acid with 50 mL of the ammonium acetate solution.

10.18. Ammonia/methanol solution, 0.1 % mass fraction. - Mix 0.4 mL of 25 % ammonia solution (10.16) with 99.6 mL of methanol (10.11).

10.19. Acetic Acid/Methanol solution – Mix 1.3 mL of Acetic Acid (10.15) with 98.7 mL methanol (10.12).

11.0 SAMPLE HANDLING AND PRESERVATION

11.1. All samples must be collected in a 250 mL HDPE bottle with a polyethylene screw cap.

11.2. Additional containers for field blanks are included with each shipment. One container is filled with reagent water and preservatives (if applicable) in the lab and shipped with field sample containers. A second empty sealed bottle (no preservatives) is included. At the sampling site, the container containing the reagent water is poured into the empty bottle and returned with the field samples.

11.3. 1.25 g Trizma must be added to the 250 mL water sample before sample collection, if applicable. This should be used for drinking water samples only.

11.4. Samples must be shipped on ice. They must be received at the lab at 10 °C or less within 48 hours of collection for waters (6 °C or less for solids). The temperature should be confirmed to be within specification when they are received. All samples stored in the lab must be stored at or below 6 °C until analysis and should not be frozen.

11.5. Upon sample receipt, drinking water samples only are checked for dechlorination. If the free chlorine is > 0.1 mg/L, samples are rejected and a new sample must be requested.

11.6. Water samples must be extracted within 14 days of collection and analyzed within 28 days after extraction. Solid samples must be extracted and analyzed within 28 days of collection for solids. Extracts must be stored at room temperature.

11.7. If samples are not in appropriate containers or holding time has expired, initiate a Nonconformance Report (DER). For instructions, refer to GL-QS-E-004 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Item.

12.0 SAMPLE PREPARATION

All batches (up to 20 samples) will be extracted with a method blank (MB), laboratory control sample (LCS), matrix spike (MS), and matrix spike duplicate (MSD). If insufficient sample is provided, the MS/MSD will be substituted with a laboratory control sample duplicate (LCSD).

13.0 EXTRACTION

13.1. See Appendix 2 for the water extraction procedure and Appendix 9 and 10 for extraction check lists

13.2. See Appendix 3 for the solids extraction procedure.

13.3. See Appendix 4 for the AFFF Procedure

14.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

14.1. Analyte standard solutions – Analyte standards may be purchased commercially as ampoulized solutions or prepared from neat materials. Purchased standards must contain linear and branched isomers, if available. PFHxS and PFOS are not available as the acids but rather as their corresponding salts, such as Na+ and K+. These salts are acceptable starting materials for the stock standards provided the measured mass is corrected for the salt content (adjusted to the anion concentration) according to the equation below. Prepare the Analyte Stock and Primary Dilutions Standards as described below.

$$\text{Mass}_{\text{acid}} = \text{Measured Mass}_{\text{salt}} \times \frac{MW_{acid}}{MW_{salt}}$$

Where:

MW_{Acid} = Molecular weight of the PFAA

MW_{Salt} = Molecular weight of the purchased salt

14.2. Standards

14.2.1. Source standard solutions are purchased from certified vendors. Standards were purchased from Wellington Labs Inc. Once opened, they are stored in HDPE containers. The standard expires on the vendor expiration date. They are stored at 4 °C. Refer to Appendix 7 and 8 of this document for standard calibration concentration levels.

14.2.2. The working and intermediate standard solutions are prepared in 80:20 (vol/vol) MeOH/water (96:4 Vol/vol MeOH/water for drinking water) from the stock standard. These solutions are stored in HDPE bottles/vials and may be used for up to 6 months from the date of preparation for working standards and up to one year for intermediate standards from the date prepared or the vendor expiration date whichever is shorter.

14.3. For guidance on standard documentation and traceability, refer to GL-LB-E-007 for Laboratory Standards Documentation.

15.0 QUALITY CONTROL REQUIREMENTS FOR PROCESSING AND EXTRACTION

15.1. QC requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing Field Samples. This section describes the QC parameters, their required frequencies, and the performance criteria that must be met in order to meet EPA quality objectives.

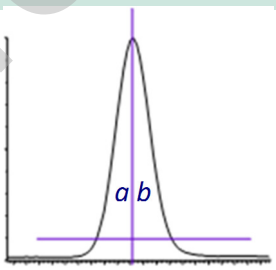
15.2. INITIAL DEMONSTRATION OF CAPABILITY – The IDOC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined in Section 17.4.

15.2.1. INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROND – Any time a new lot of SPE cartridges, solvents, centrifuge tubes, disposable pipets, and autosampler vials are used, it must be demonstrated that a method blank is reasonably free of contamination and that the criteria in Section 18.1.4 are met.

15.2.2. INITIAL DEMONSTRATION OF PRECISION (IDP) – Prepare, extract, and analyze four to seven replicate LCSs spiked near the midrange of the initial calibration curve according to the procedure described in Appendix 2 or 3. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

15.2.3. INITIAL DEMONSTRATION OF ACCURACY (IDA) - Using the same set of replicate data generated for Section 15.2.2, calculate average recovery. The average recovery of the replicate values must be within ± 30% of the true value.

15.2.4. INITIAL DEMONSTRATION OF PEAK ASYMMETRY FACTOR (IDPA) - A peak asymmetry factor must be calculated using the equation below during the IDL and every time a calibration curve is generated. The peak asymmetry factor for the first two eluting peaks in a mid- level CAL standard must fall in the range of 0.8 to 1.5. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted. This measurement is performed by the instrument software.



$$A_s = \frac{B}{A}$$

Where:

A_s = Peak asymmetry factor

B = Width of back half of the peak measured (at 10% peak height) from the trailing edge of the peak to a line dropped perpendicularly from the peak apex

a = The width of the front half of the peak measured (at 10% peak height) from the leading edge of the peak to a line dropped perpendicularly from the apex.

15.2.5. MINIMUM REPORTING LEVEL (MRL) Confirmation - The lowest CAL standard used to establish the Initial Calibration will be at or below the concentration of the MRL. See LOQ.

15.2.6. CALIBRATION CONFIRMATION – Analyze an ICV as described in Section 17.5.1.1 to confirm the accuracy of the standards/calibration curve.

15.2.7. DETECTION LIMIT DETERMINATION – The minimum concentration of an analyte that can be measured, identified and reported with 99% confidence that the concentration is greater than zero. This is a statistical determination of precision, and accurate quantitation is not expected at this level.

15.3. On-going QC Requirements- This section summarizes the ongoing QC criteria that must be followed when processing and analyzing wastewater and solid samples. See Appendix 6 for ongoing QC criteria for drinking water samples.

15.3.1. CONTINUING CALIBRATION VERIFICATION (CCV) - CCV standards are analyzed at the beginning of each analysis batch, after every 10 field samples, and at the end of the analysis batch. See Section 17.5.2 for acceptance criteria solid and water and Appendix 1.

15.3.2. INJECTED INTERNAL STANDARDS (IS)- The analyst must monitor the peak areas of the IS(s) in all injections during each analysis day. On days when the initial calibration standards were analyzed, the IS responses (peak areas) in any chromatographic run must not deviate by more than 50% from the area measured in the midpoint standard of the initial calibration. On days when the ICAL is not performed, the peak area must not deviate by more than 50% from the area measured in the daily initial CCV.

15.3.2.1. If the IS areas in a chromatographic run do not meet these criteria, inject a second aliquot of that extract aliquoted into a new capped autosampler vial. Random evaporation losses have been observed with the snap caps causing high IS(s)

areas. If the reinjected aliquot produces an acceptable IS response, report results for that aliquot.

15.3.2.2. If the reinjected extract fails again, either analysis may be reported with the appropriate flags. The failure must also be discussed in the case narrative. Alternatively, collect a new sample and re-analyze.

15.3.3. FIELD REAGENT BLANK (FRB) – The purpose of the FRB is to ensure that PFAAs measured in the samples were not inadvertently introduced into the sample during sample collection/handling. The FRB is processed, extracted and analyzed in exactly the same manner as a sample. For drinking waters, if the method analyte(s) found in the sample is present in the FRB at a concentration greater than ½ LOQ, then all samples collected with that FRB are invalid and must be recollected and reanalyzed.

15.3.4. INITIAL CALIBRATION VERIFICATION (ICV) – An ICV is a standard from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard from the same vendor should be used. The ICV should be prepared and analyzed just like a CCV. Acceptance criteria for the ICV are identical to the CCVs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem. This standard is analyzed whenever a new initial calibration curve is analyzed.

15.3.5. INSTRUMENT SENSITIVITY CHECK (ISC) – A standard spiked at the lowest level of the calibration curve (LOQ). The calculated amount for each analyte must be ± 30% of the expected value. It should be analyzed prior to sample analysis and at least every 12 hours. The ISC can be used as the initial CCV of the day.

16.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

16.1. Maintenance for the LCMSMS

16.1.1. Daily Maintenance

16.1.1.1. Solvents: Adequate volume of solvent needs to be maintained on a daily basis. Failure to do so may result in loss of prime on the LC. This is especially important for the needle wash solvent. Make sure that there is plenty of solvent in each reservoir before using. When a long acquisition run is set up, it is essential to calculate the amount of solvent that will be

needed. Add an extra 20% of solvent to the reservoir to make sure the LC does not go dry during the run.

16.1.1.2. Column: The column must be properly equilibrated with the method specific solvent before batch analysis can occur. At the end of the day or an analysis, the column must be flushed with solvent, usually acetonitrile or methanol, to ensure longevity.

16.1.1.3. Syringe: Check the operation of the sample syringe on a daily basis to ensure the syringe is drawing the proper amount of sample. Make sure the syringe is free of bubbles and that the needle is injecting properly.

16.1.1.4. Solvent Lines and Pump: Prime the system as needed to ensure proper solvent flow to the column.

16.2. Weekly Maintenance

16.2.1. Waste Container: Check the waste container and dispose if needed. The satellite waste container should never be more than ¾ full. Always label waste properly.

16.3. Semi-Annual Maintenance

16.3.1. Plunger seals: Inspect the plunger and plunger seals. If the pump has been losing prime or if the ripple delta is greater than 30 psi, the seals will need to be replaced.

16.3.2. Syringe and injector. Inspect the syringe and injector needle. Replace needle if it is bent or damaged. Replace syringe if there are obvious signs of wear.

16.4. Maintenance for the Mass Spectrometer

16.4.1. Vacuum System Maintenance

16.4.1.1. Daily Maintenance

16.4.1.1.1. Rotary Pumps: The Agilent MS 40+ pump, which backs the quadrupoles. Make sure oil levels in the pumps are sufficient on a daily basis. Check for any leaks.

16.4.2. Mass Spectrometer Source Maintenance

16.4.2.1. Clean the orifice and skimmer plate when discoloration appears.

16.4.2.2. Refer to the AB SCIEX Manual for other required maintenance

16.5. ESI Probe Maintenance

16.5.1. The ESI probe needs to be maintained at all times to ensure maximum sensitivity. Problems that may inform an analyst of needed maintenance are: an unstable ion beam (spray), peak broadening or tailing, low LC pump back pressure, high LC pump back pressure, or gas flow problems. Refer to the manual for troubleshooting tips.

16.5.2. The probe tip may need to be cleaned if dirty matrices are run, especially at low heater temperatures.

17.0 INSTRUMENT CALIBRATION

17.1. A mass calibration is performed initially prior to use. It should be verified before calibration and updated on an as- needed basis (e.g., QC failures, after major preventative maintenance). Refer to the manufacturer's instructions for instrument tuning and conditions.

17.2. Mass Spectral Acquisition Rate – A minimum of 10 spectra scans are acquired across each chromatographic peak for each analyte, Extracted Internal Standard and Injected Internal Standard.

17.3. Ion Transitions (Parent →Product) – Prior to method implementation, the chemical derivation of the ion transitions used for quantitation and confirmation must be documented for all analytes except PFBA and PFPeA. The ion transition ratio per analyte should also be documented and monitored. Please see Table 2 for the transitions used for each analyte, ES and IS.

17.4. Initial Calibration Curve

17.4.1. Isotope Dilution Quantitation must be used for this analysis. The isotopically labeled analog of each analyte (Extracted Internal Standard) must be used if commercially available. If a labeled analog is not available, the Extracted Internal standard with the closest retention time to the analyte should be used (Internal Standard Quantitation).

NOTE: Isotope Dilution Quantitation should not be used when analyzing drinking water samples. See Appendix 6 for drinking water calibration criteria.

17.4.2. A minimum of five calibration points is required for this analysis unless a second order regression fit is used. If a second order fit is used, six calibration standards are required. If analyzing drinking waters, the curves must be forced through zero. See Appendix 7 for ground water calibration concentration levels. See Appendix 8 for drinking water calibration concentration levels.

17.4.3. When quantitated using the initial calibration curve, the calibration point for each analyte must calculate to be within 70-130% of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action is taken to

reanalyze the CAL standards, restrict the range of calibration, or select an alternate method of calibration.

CAUTION: When acquiring MS/MS data, LC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the segment time window.

17.4.4. When an internal standard is used, the ratio of the area response of the target to the area response of the nearest internal standard is used. The Injected Internal Standard area count for each point in the ICAL should fall within -50% to +50% of the area measured in midpoint of the ICAL standard. The Extracted Internal Standard area count for each point in the ICAL should fall within -50% to +50% of the average area measured in all ICAL standards.

17.4.5. Calibrations are modeled as average response factor and calibration curves. For average response factor the %RSD must be ≤ 20%. For least-square linear regression fits, unweighted, 1/X or $1/X^2$ weighting can be used. The correlation coefficient (r) must be ≥ 0.995 unless otherwise stated. For second order regression fits, weighting can be used and the coefficient of determination (r^2) must be ≥ 0.990 unless otherwise stated. While second-order regression equations may be used, the intercept and degree of curvature should be examined to be sure that results would be reliable throughout the range of the curve.

17.4.6. Generally, it is not acceptable to remove points from a calibration for the purpose of meeting calibration criteria, unless the points are at the high or low ends of the curve. If a point is removed from the low end, the reporting limit may be adjusted accordingly. If a point is removed from the high end, the linear calibration range must be adjusted accordingly. Whenever a point is removed, it must be clearly documented on the instrument log.

17.4.7. If there is a problem with the calibration that appears to be associated with a single standard, that one standard may be re-analyzed. The calibration function would then be recalculated against the acceptance criteria. If the criteria still cannot be met, then the entire initial calibration should be performed again. An initial calibration should be considered a single event. Therefore, the re-analysis of a calibration standard should be performed immediately to ensure that the reanalysis is still part of the original initial calibration event, and before any samples are analyzed.

17.4.8. All initial calibration points must be analyzed without any changes to instrument conditions.

17.5. Initial and Continuing Calibration Verification

17.5.1. Initial Calibration Verification (ICV)

17.5.1.1. An ICV standard is analyzed following the analysis of a new initial calibration, and must be created from a second source standard. The acceptance limits are 70-130%. See Appendix 6 for criteria used for drinking water analysis.

17.5.2. Continuing Calibration Verification (CCV)

17.5.2.1. Verify the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. In this context, a "sample" is considered to be a field sample. MBs, CCVs, LCSs, MSs, FDs, FRBs and MSDs are not counted as samples.

17.5.2.2. The beginning CCV of each analysis batch must be at or below the LOQ in order to verify instrument sensitivity prior to any analyses. If standards have been prepared such that all low ICAL points are not in the same solution, it may be necessary to analyze two standards to meet this requirement. Analyte concentrations in subsequent CCVs must range from the LOQ to the mid-level calibration concentration. These low level standards must be analyzed every 12 hours.

17.5.2.3. Inject an aliquot of the appropriate concentration CAL standard and analyze with the same conditions used during the initial calibration.

17.5.2.4. Determine that the absolute areas of the quantitation ions of the IS(s) meet the acceptance criterion for each analyte. If any of the IS areas do not fall within the acceptance criterion, adjustments must be made to restore system sensitivity. These adjustments may include cleaning of the MS ion source, or other maintenance as indicated in Section 16.4. Major instrument maintenance requires recalibration and verification of sensitivity by analyzing a CCV at or below the LOQ.

17.5.2.5. Calculate the concentration of each analyte in the CCV. The calculated amount for each analyte must be within ±30% of the true value (±50% if analyzing for drinking water samples). If these conditions do not exist, then all data for the problem analyte must be considered invalid, and one of the following remedial action should be taken.

17.5.2.5.1. Samples analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception. If the CCV fails because the calculated concentration is greater than 130% for any analyte, and sample extracts show no detection for that analyte, non- detects may be reported without re-analysis.

17.5.2.5.2. Immediately analyze two additional consecutive CCVs. If both CCVs pass, samples may be reported without re-analysis. If either fails, or if two consecutive CCVs cannot be analyzed, perform corrective action(s) and re-analyze the CCV and all associated samples since the last acceptable CCV.

17.6. Instrument Blanks (IB)

17.6.1. A solvent blank is analyzed immediately following the highest standard analyzed and daily prior to sample analysis. The concentration of each target must be ≤ ½ LOQ.

NOTE: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. The highest standard may be a part of the calibration curve or following the calibration curve. If analyzed following the calibration curve, it can only be used to document the highest concentration at which carryover does not occur and cannot be used to extend out the calibration curve range. If sample concentrations exceed this range and the sample(s) following exceed the acceptance criteria, they must be re-analyzed.

17.6.1.1. If target analytes are less than the acceptance criteria, calibration must be performed using a lower concentration for the highest standard until the acceptance criterion is met. If acceptance criteria are not met after the highest standard which is not included in the calibration curve, the standard cannot be used to determine the highest concentration in samples at which carryover does not occur.

17.6.1.2. If acceptance criteria are not met after samples, additional instrument blanks must be analyzed until acceptance criteria are met. Additional samples should not be analyzed until the acceptance criteria are met.

18.0 ANALYTICAL QUALITY CONTROL REQUIREMENTS AND CONTINGENCIES

18.1.1. Method Blank (MB)

18.1.2. MB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing.

18.1.3. When samples that are extracted together are analyzed on separate instruments or days, the method blank associated with those samples must be analyzed on at least one of those instruments and/or days. A solvent blank should be analyzed on all other instruments/days on which any of the samples are analyzed.

18.1.4. The MB must not exhibit values that exceed the 1/2 Limit of Quantitation (LOQ) (1/3 LOQ for drinking waters) for any target analyte. MB values > 1/2 LOQ (1/3 LOQ for drinking waters) indicate laboratory or reagent contamination should be suspected. (See Appendix 6 for all drinking water criteria):

18.1.4.1. The MB may be reanalyzed once to determine if the contamination is instrument related (carryover, etc.). If the reanalysis confirms an instrument-related problem and that the MB has not been contaminated, analysis may proceed.

18.1.4.2. Upon confirmation of the contamination, samples exhibiting positively detected analytes (i.e., greater than the LOQ) that were also detected in the associated MB may be reported if the sample results are at least 10 times the concentration detected in the MB.

18.1.4.3. Samples exhibiting positively detected analytes (i.e., greater than the LOQ) that were also detected in the associated MB but are less than 10 times the concentration detected in the MB must be re-extracted and re-analyzed.

18.1.4.4. If there is insufficient sample volume remaining, or if the holding time has expired, the client must be consulted prior to beginning re-extraction. The deficiency must be documented.

18.2. Laboratory Control Sample (LCS)

18.2.1. The LCS consists of an aliquot of blank matrix that is spiked with the same analytes at the same concentration as the matrix spike sample. The LCS is used to assess the ability of the analytical system to produce acceptable results and undergoes all sample treatments that the associated samples undergo

Calculate the percent recovery (%R) for each target analyte using the following equation:

$$\%R = \frac{\text{Found Value} \times 100}{\text{True Value}}$$

18.2.2. An LCS is required with each extraction batch. It will be spiked at, or less than, the midpoint of the ICAL. Recoveries must fall within the DoD/DOE QSM limits. If the LCS results do not meet these criteria for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. If the recovery of any analyte falls outside the established control limits, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing the analyses.

The following corrective actions are recommended:

18.2.2.1. The LCS may be reanalyzed once to determine if the out of control result is instrument related. If upon reanalysis the out of control analytes are in control, analysis and reporting of the associated samples may proceed.

18.2.2.2. If the %R for any analyte in the LCS is below the lower control limit, or if the %R is above the upper control and the analyte was detected in the associated samples above the LOQ, all associated samples must be re-extracted and re-analyzed for that analyte.

NOTE: If there is insufficient sample volume remaining or if the holding time has expired for any sample associated with the LCS, the client must be consulted prior to beginning re-extraction. The deficiency must be fully documented and it must be noted in the final report.

18.2.2.3. If the %R for any analyte in the LCS is above the upper control limit, and the associated samples do not exhibit concentrations above the LOQ for that analyte, the sample results may be reported. This indicates a high bias may exist for the batch for that analyte, but since the samples were free of detections, the potential high bias does not affect the sample result. The deficiency must be documented and noted in the final report.

18.3. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

18.3.1. A matrix spike is a sample that is spiked with the target analytes and is used to assess the effect of the matrix on the target analytes. If there is insufficient sample volume to prepare a MSD or a sample duplicate, a LCSD must be prepared and analyzed. The accuracy of the MS and MSD is reported as %R and is calculated as follows:

$$\%R = \frac{C_s - C}{S} * 100$$

Where:

%R =	Percent recovery
C_s =	Spiked sample concentration
C =	Unspiked concentration
S =	Concentration of the spike added to the sample

18.3.2. The MSD, sample duplicate or LCSD is used to measure the precision of the analytical system. The precision is expressed as relative percent difference (RPD), and is calculated using the following equation:

$$RPD = \frac{|a - b|}{[(a + b)/2]} \times 100$$

Where:

RPD =	Relative Percent Difference
a =	Result of MS, sample or LCS
b =	Result of MSD, sample duplicate or LCSD

18.3.3. The %R should fall within the DOD QSM limits for all matrices except drinking water. Drinking water recoveries should be between 70%-130%. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCVs, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is qualified and a statement made in the case narrative to notify the end user that the results are suspect due to matrix effects. Also, look for objective evidence of matrix interference such as sample heterogeneity, chromatographic behavior, LCS recoveries, method blank, required dilutions or behavior of the sample during extraction. MS, MSD or MS/MSD RPD failures and sample matrix observations must be documented.

18.3.4. RPDs for MSDs, sample duplicate or LCSD should be ≤30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of 2 of the LOQ. At these concentrations, FDs should have RPDs that are ≤50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the LCS, the recovery is judged to be matrix

biased. The result for that analyte in the unfortified sample is appropriately qualified and the issue of the results being suspect due to matrix effects documented in the case.

18.4. Extracted Internal Standards

18.4.1. The ES is the isotopically labeled analog of the analyte being analyzed, when available. It is spiked into all samples (except drinking waters) in the batch, including QC samples prior to extraction. The recovery is used to assess the effectiveness of the extraction procedure and matrix effects. Recoveries must be in the range of 50-150% of the true value.

18.4.2. If the recoveries are not within the control limits for the MB, LCS or LCSD, and/or samples, the following corrective actions are recommended:

18.4.2.1. The extract may be reanalyzed to determine if the out of control result is instrument related. If upon reanalysis the criterion is met, analysis and reporting of the associated samples may proceed.

18.4.2.2. If the %R is outside the control limits, all associated samples may be re-prepped and re-analyzed for that analyte (greater dilution may be needed). If there is insufficient sample volume remaining or if the holding time has expired for any associated sample, the client must be consulted prior to beginning re-extraction.

18.4.2.3. The sample can also be diluted and re-analyzed to remove the matrix interference. If this option is chosen, additional ES standard must be added to the diluted sample.

19.0 CALCULATIONS

19.1. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound is the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_X C_{IS}) / (A_{IS} C_X)$$

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.

C_X = Concentration of the compound being measured.

19.2. The average RF must be calculated for each compound.

19.3. The percent relative standard deviation (%RSD) should be less than 20% for each analyte.

$$\%RSD = \frac{SD}{RF} x100$$

Where:

$\overline{RF}$ = Mean of RFs from initial calibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound

$$SD = \sqrt{\sum_{c=1}^{n} \frac{\left(x_1 - \bar{x}\right)^2}{N-1}}$$

19.4. Continuing Calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} x100\%$$

Where:

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

19.5. Concentration in the Extract

The concentration of each identified analyte and Injected IS in the extract is calculated by average response factor or a regression fit.

19.5.1. Linear fit

$$C_{ex} = A + B\frac{(R_X C_{IS})}{R_{IS}} \qquad C_{ex} = \frac{(R_X - A)}{B}$$

Where:

C_{ex} = Concentration in the extract

C_{is} = Concentration of the Internal Standard

R_x = Response for the analyte
R_{IS} = Response for the Injected IS
A = Intercept
B = Slope

19.5.2. Quadratic Fit

Instrument data reduction software performs the quadratic equation that has been validated by the Quality department. For more information refer to the owner's manuals or contact the instrument's manufacturer.

19.5.3. Average response factor

$$C_{ex} = \frac{(A_X C_{IS})}{(A_{IS} \overline{RF})}$$

Where:

C_{ex} = Concentration in extract
C_{IS} = Concentration of internal standard
$\overline{RF}$ = Average RF
A_x = Area of the extract
A_{IS} = Area of the internal standard

19.5.3.1. Concentration Determination of an Aqueous Sample

$(ng/L) = (C_{ex})(V_t)(D_f)/(V_o)$

Where:

C_{ex} = Concentration found in the extract in ng/L
V_t = Final Volume of the extract in mL
D_f = Dilution Factor.
V_o = Volume of water extracted (mL).

19.5.3.2. Sediment/Soil Sludge (on a dry-weight basis) and Waste and Tissue (normally on a wet-weight or as received basis):

Concentration

$(ng/Kg) = (C_{ex})(V_t)(D_f)/(W_s)(D)$

Where:

C_{ex},V_t, Ais, D_f = Same as for water matrix

Ws = Weight of sample in grams.

D = (100% - moisture in sample)/100, or 1 for wet-weight basis.

19.6. LCS Percent Recovery

$$LCS\ \text{Recovery} = \frac{SSR}{SA} X100$$

Where:

SSR = Spike Sample Result

SA = Spike added

19.7. MS/MSD Spike Recovery calculations

$$MatrixSpike\ \text{Recovery} = \frac{SSR - SR}{SA} X100$$

Where:

SSR = Spike Sample Result

SA = Spike Added

SR = Sample Result

19.8. Relative Percent Difference calculation for the MS/MSD or sample/sample duplicate.

$$RPD = \frac{MS_R - MSD_R}{\frac{1}{2}(MS_R + MSD_R)} X100$$

Where:

RPD = Relative Percent Difference

MS_R = Matrix Spike Result or Sample Spike Result

MSD_R = Matrix Spike Duplicate Result or Sample Spike Duplicate Result

20.0 INSTRUMENT PERFORMANCE REQUIREMENTS

See Appendix 1 for all criteria.

21.0 ANALYST AND METHOD VALIDATION REQUIREMENTS

21.1. To establish that the analyst can perform the procedures in an acceptable manner and that the method generates data of acceptable bias and precision, the following operations are performed.

21.1.1. A quality control (QC) check standard must be prepared containing each analyte of interest. It must be prepared from pure standard material or purchased as a certified solution. It must be made from a source independent of that used for calibration if commercially available.

21.1.2. Four samples must be prepared and analyzed by the same procedures used to prepare and analyze actual samples.

21.1.3. Calculate the average recovery (X) in ng/L, and the standard deviation of the recovery (S) in ng/L, for each analyte of interest using the four results.

21.1.4. For each analyte compare S and X with the corresponding acceptance criteria for precision and accuracy, respectively, given in the quality control table at the end of the method. If the S and X for all analytes of interest meet the acceptance criteria, the system's performance is acceptable and analysis of actual samples can begin. If any individual S and X exceeds the precision limits or falls out of the range for accuracy, the system's performance is unacceptable for that analyte and a check standard for that analyte must be prepared and reanalyzed.

21.2. Method detection limits are also determined and documented annually. Aqueous method detection limits and verifications are performed as stated in the GL-LB-E-001 for the Determination of Method Detection Limits. Typical MDLs for this method are 0.67 ng/L for waters and 166 ng/Kg for solids.

21.3. Precision and accuracy are matrix dependent and are documented by means of a laboratory control sample (LCS) and a matrix spike and matrix spike duplicate.

22.0 INSTRUMENT PROCEDURES AND QUALITY CONTROL

22.1. Before sample analysis begins, the instrument must have acceptable calibration curves. Each Curve is verified by the analysis of second source continuing calibration standards. Each standard must meet the acceptance criteria for percent difference or drift. Continuing calibration verification standards must be analyzed after every ten samples.

22.2. If the analyte of interest is present at a concentration between the MDL and RL, all data are qualified with a "J" flag and reported. If the analyte of interest is present at a concentration above the RL and the samples contain the analyte of interest at a concentration of greater than 10 times the concentration found in the blank, the data

are qualified with a "B" flag and reported. If the concentration found in the sample is less than 10 times that found in the blank and greater than the RL, the samples must be re-extracted. If the samples do not contain the analytes of interest, the data are reported.

22.3. Nonconformance

22.3.1. When analyzing a calibration curve for more than one analyte at a time, some of the analytes may not meet the acceptance criteria. Additional standards containing the compounds that were not acceptable may be analyzed. If the curve still does not meet the acceptance criteria, maintenance should be performed or a new standard may be needed.

22.3.2. If the continuing check standard fails any of the criteria, the analyst must take action to correct the situation. This may be performing any of the maintenance steps described in the appropriate SOP to get the instrument to meet its daily calibration. If all attempts fail, the analyst must analyze a new series of calibration standards, thus obtaining a new calibration curve.

22.3.3. If the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed. If an analyte above the QC limits was detected in a sample extract, reinjection of the extract is necessary.

23.0 DATA RECORDING

Data are recorded and calculated by the instrument data acquisition system. They are stored on a remote server. The data are also entered into the Laboratory Information Management System (AlphaLIMS).

24.0 RECORDS MANAGEMENT

24.1. Documentation of Training

Extraction technicians and analysts must be properly trained to perform the contents of this SOP. Personnel will extract or analyze four laboratory control samples for this SOP as training commences. Training is documented per GL-HR-E-003 for Maintaining Technical Training Records.

24.2. Documentation of Extraction

24.2.1. In AlphaLIMS, complete the Sample Tracker Form. Record initial weight of the sample, final volume of the extract, amount of ES and spikes added, and any comments about the extraction process. Also, record all reagent lot numbers and note any deviation from this standard operating procedure.

24.2.2. Print a hard copy to submit with the extracts

24.2.3. Have the batch peer reviewed.

24.2.4. All documents are stored in AlphaLIMS.

24.3. Documentation of Standards

Refer to GL-LB-E-007 for Laboratory Standards Documentation.

25.0 DATA REVIEW, APPROVAL AND TRANSMITTAL FOR EXTRACTION AND ANALYTICAL GROUPS

25.1. Extraction Group: A review process is used to ensure the quality of the data. Extraction logs are peer reviewed by a second technician or Group Leader. When the reviewer is satisfied that the data have been entered correctly, a data report is generated from AlphaLIMS. The report along with the batch sheets are copied and submitted to the appropriate analytical area for analysis.

25.2. Analytical Group

25.2.1. Levels of review and their responsibilities

25.2.1.1. First level review - The analyst must check all chromatograms. They will also ensure that the percent recoveries for the spike, duplicate, and all IS recoveries are acceptable. They must check to see if the check standard passes for the analytes of interest. The peak's shape must also be checked to ensure that it is indeed a peak and not noise. If the detect meets all requirements (see Appendix 1 for DOD QSM criteria), its concentration should be reported. Upon completion of a batch, the analyst enters the data. A data report is generated and it is placed in a folder along with the batch and all other raw data (chromatograms). This folder is given to the peer review analyst for reviewing.

25.2.1.2. Second level review - The data validator or other qualified reviewer must ensure that the concentration that appears in the external standards table is indeed what has been entered into the computer. They must check to see if the calibration check standard is acceptable and if the LCS and its duplicate and the ISs are all within acceptable ranges. The reviewer must also check the date analyzed, dilution factor, and time of analysis from the raw data against the data report. If everything is acceptable, the reviewer must then initial and date the data report. The data report is then sent to a status of "Done."

25.2.1.3. To complete a review process, all chromatograms of the calibration check standard, blank, LCS and its duplicate, samples and the spike and/or duplicates of the sample must be

present. The batch sheet, sample tracker log, and the data report should all be present.

25.2.1.4. Refer to SOP GL-OA-E-044, Organics Data Validation for additional information on validation.

26.0 METHOD VERIFICATION AND VARIATION

26.1. This procedure deviates from EPA 537.1 for waste water and solid analysis only by using Isotope Dilution to calculate analyte concentrations in place of internal standards. We refer to these isotopes as Extraction Internal Standards. The Injected Internal Standards are added to the samples and QC prior to extraction in place of surrogates.

26.2. This procedure deviates from EPA 537.1 for waste water and solid analysis only by using 80:20 methanol/water (vol/vol) as the final solvent for standards and samples instead of the method prescribed 96:4 methanol/water solvent when extracting samples other than drinking waters.

26.3. This procedure deviates from EPA 537.1 for waste water and solid analysis only by not forcing the calibration curves through zero when analyzing non-drinking water samples. However, each individual point must meet the 70%-130% recovery criteria.

26.4. The Method Detection Limit studies were performed in accordance with GL-LB-E-001for the Determination of Method Detection Limits.

26.5. Per EPA 537.1, the IS must deviate no more than ± 50% of the initial calibration and must fall within 70% - 140% of the most recent CCV. This criterion is used for drinking water samples only. For all matrices other than drinking water, the Injection Internal Standard recovery criterion differs in that on days when the initial calibration standards were analyzed, the IS responses (peak areas) in any chromatographic run must not deviate by more than ± 50% from the area measured in the midpoint standard of the initial calibration. On days when the calibration is not performed, the peak area must not deviate by more than ± 50% from the area measured in the daily initial CCV.

27.0 REFERENCES

27.1. EPA Method 537.1 Determination of Selected Perfluorinated alkyl acids in drinking water by Solid Phase Extraction and liquid chromatography/tandem mass spectrometry (LC/MC/MS) Version 1.1, September 200.9 National Exposure Research Laboratory Office of Research and Development U. S. Environmental Protection agency Cincinnati, Ohio 45268.

27.2. ISO (2009)ISO 25101:2009(E)Water Quality- Determination of perfluorooctanesulfonate (PFOS) and perfluorooctonate (PFOA)-Method for unfiltered sample using solid phase extraction and liquid chromatography/mass spectrometry. First Edition 2009-03-01.

27.3. ASTM D7979-17 Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS).

27.4. ASTM D7968-17a Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS).

27.5. Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3, May, 2019.

27.6. Dept. of Defense (DOD) Bottle Selection and other Sampling Considerations When Sampling for Per-and Poly-Fluoroalkyl Substances (PFASs), Rev. 1.1, Oct 2016.

27.7. EPA Method 537.1 Version 1.0. Determination of Selected Perfluorinated alkyl acids in drinking water by Solid Phase Extraction and liquid chromatography/tandem mass spectrometry (LC/MC/MS), November 2018 National Exposure Research Laboratory Office of Research and Development U. S. Environmental Protection agency Cincinnati, Ohio 45268.

28.0 WASTE MANAGEMENT

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001

29.0 HISTORY

Revision 7: Updated for DoD QSM Version 5.3 changes and added Appendix 9 and 10.

Revision 6: Revised to appropriately reference Appendices 7 and 8. Update Appendix header for consistency. Revised standards expiration date usage.

Revision 5: Added Calibration Concentration Chart (Appendix 7) and added new compounds and Appendix 8. Added tissue as additional matrix for analysis.

Revision 4: Revised to clarify AFFF criteria.

Revision 3: Revised to add clarification pertaining to MB and LOQ. Updated References section.

APPENDIX 1: DOD/DOE QSM 5.3 QC REQUIREMENTS

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Aqueous Sample Preparation	Each sample and associated batch QC samples.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., AFFF formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilutions be performed in duplicate. Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE.	NA.	NA.	Samples with >1% solids may require centrifugation prior to SPE extraction. Pre-screening of separate aliquots of aqueous samples is recommended.
Solid Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling	NA.	NA.	NA.
Biota Sample Preparation	Each sample and associated batch QC samples.	Sample prepared as defined by the project (e.g., whole fish versus filleted fish).	NA.	NA.	NA.
AFFF and AFFF Mixture Sample Preparation	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate). Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	NA.	NA.	Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF formulation samples.	ENVI-Carb™ or equivalent must be used on each sample and batch QC sample.	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix Interferences.
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to initial calibration (ICAL).	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 amu of the true value, by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer on corrective maintenance	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under failing mass calibration. The mass calibration is updated on a as-needed basis (e.g., QC failures, ion masses fall outside of the ±0.5 amu of the true value, major instrument maintenance is performed, or the instrument is moved).
Mass Spectral Acquisition Rate	Each analyte, Extracted Internal Standard (EIS) Analyte	A minimum of 10 spectra scans are acquired across each chromatographic peak.	NA.	Flagging is not appropriate.	NA.
Calibration, Calibration Verification, and Spiking Standards	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes. For PFAS that do not have a quantitative branched and linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and	NA.	Flagging is not appropriate.	Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e. accounting for peaks that are identified as linear and branched isomers) and relying on the initial calibration that uses the linear isomer quantitative standard.			quantitative analysis.
Sample PFAS Identification	All analytes detected in a sample.	The chemical derivation of the ion transitions must be documented. A minimum of two ion transitions (Precursor → quant ion and precursor → confirmation ion) and the ion transitions ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50-150%. Signal to Noise Ratio (S/N) must be ≥ 10 for all ions used for quantification and must be ≥ 3 for all ions used for confirmation. Quant ion and confirmation ion must be present and must maximize simultaneously (± 2 seconds).	NA.	PFAS identified with ion ratios that fail acceptance criteria must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as "estimated, biased high".	For example: Ion Ratio = (quant ion abundance/confirm ion abundance) Calculate the average ratio (A) and standard deviation (SD) suing the ICAL standards. An acceptance range of ratio could be within A ±3SD for confirmation of detection.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Ion Transitions (Precursor-> Product)	Every field sample, standard, blank, and QC sample.	In order to avoid biasing results high due to known interferences for some transitions, the following transitions must be used for the quantification of the following analytes: PFOA: 413 —› 369 PFOS: 499 —› 80 PFHxS: 399 —› 80 PFBS: 299 —› 80 4:2 FTS: 327 —› 307 6:2 FTS: 427 —› 407 8:2 FTS: 527 —› 507 NEtFOSAA: 584 —› 419 NMeFOSAA: 570 —› 419 If these transitions are not used, the reason must be technically justified and documented (e.g., alternate transition was used due to observed interferences).	NA.	Flagging is not appropriate.	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	The isotopically labeled analog of an analyte (Extracted Internal Standard Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts are acceptable providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number. If a labeled analog is not commercially available, the Extracted Internal Standard Analyte with the closest retention time or chemical similarity to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70-130% of their true value for each calibration standard. ICAL must meet one of the two options below: Option 1: The RSD of the RFs for all analytes must be ≤ 20%. Option 2: Linear or non-linear calibrations must have r^2 ≥0.99 for each analyte.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ICAL has passed. External Calibration is not allowed for any analyte. Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed.
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.	Calculated for each analyte and EIS.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Retention Time (RT) window width	Every field sample, standard, blank, and QC sample	RT of each analyte and EIS analyte must fall within 0.4 minutes of the predicted retention times from the daily calibration verification or on days when ICAL is performed, from the midpoint standard of the ICAL. Anaytes must elute within 0.1 minutes of the associated EIS. This criterion applies only to analyte and labeled analog pairs	Correct problem and reanalyze samples	NA.	Calculated for each analyte and EIS.
Instrument Sensitivity Check (ISC)	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true value.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Instrument Sensitivity Check (ISC) can serve as a bracketing CCV.
Instrument Blanks	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument Blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (> ½ LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left.	No sample shall be analyzed until instrument blank has met acceptance criteria. Note: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
					is used only to document a higher concentration at which carryover still does not occur.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Extracted Internal Standard Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. Extracted Internal Standard Analyte recoveries must be within 50% to150% of the ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner.	Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, standard and blank, if the EIS is fortified at excessive concentrations.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, re-extract and reanalyze MB and all QC samples and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of the hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid MB. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. 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).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in0house LCS limits if project limits are not specified. RPD ≤ 30 % (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample ≥ LOQ. The MD is a second aliquot of the field sample that has been prepared by serial dilution.
Post Spike Sample	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of <LOQ for analyte(s).	Spike all analytes reported as <LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample a <LOQ. When analyte concentrations are calculated as < LOQ, the post spike for that analyte must recover within 70-130% of its true value.	When analyte concentrations are calculated as < LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.	Flagging is not appropriate.	When analyte concentrations are calculated as <LOQ, results may not be reported without acceptable post spike recoveries.

APPENDIX 2: WATER EXTRACTION

1.0 Setup:

1.1. Weigh the sample container to the nearest 1 g.

1.2. Shake the container for several minutes, with the cap tightly sealed, to ensure that any particulate matter is evenly distributed.

1.3. Prepare a Method Blank (MB) and a Laboratory Control Sample (LCS) from a 250 mL volume of organic-free reagent water, or a volume of reagent water similar to that being used for the samples in HDPE containers.

1.4. Add 125 uL of a 10 ug/L ES Standard to the samples in their original containers, the MB, LCS, and any Matrix Spikes associated to the extraction batch.

Note: If these are drinking water samples, use 125 uL of the 10 ug/L IS standard.

1.5. Add 250 uL of a 20 ug/L Spike intermediate standard to the LCS, MS and MSD in their original containers.

1.6. Shake the samples then allow to stand for several minutes. This allows the surrogate and spikes time to disperse in the samples, and will allow any particulate matter to settle.

2.0 Cartridge Conditioning:

2.1. Attach the SPE cartridge to the top of the manifold.

2.2. Fill the cartridge with 4 mL of ammonia/methanol solution. Pull the solvent through the sorbent bed. Do **not** allow the cartridge to go dry.

2.3. With a thin layer of solvent above the sorbent bed, add 4 mL of methanol. Allow the methanol to flow through the sorbent bed.

2.4. 4 mL of water is then added. Allow the water to flow through the sorbent bed. Stop the flow just before the cartridge goes dry. Close the manifold valve.

2.5. Dispose the discarded rinse solvents in the appropriate waste drum.

3.0 Sample Loading onto SPE Cartridge:

3.1. Attach a tube adapter with a polyethylene sample reservoir line to the top of the cartridge. Insert weighted end into sample container.

3.2. Engage the vacuum system to draw the sample through the cartridge a rate of approximately 10mL/min, until all of the sample has passed through the cartridge. Do **not** allow the cartridge to go dry until all of the sample has passed through it. If a cartridge runs dry, the preparation technician will notify the Group leader, and place a notation in the extraction log.

APPENDIX 2: WATER EXTRACTION - CONTINUED

3.3. Once all of the sample has loaded, rinse the bottle with 4 mL of reagent water. Allow the reagent water to pass through the transfer tubes onto the cartridge. Allow the cartridge to go dry at the end of the transfer. Discard this eluate.

3.4. Rinse the bottle with 4 mL of acetate buffer and transfer to the dried cartridge via the transfer lines. Apply a vacuum to completely remove the residual solution from the cartridge allowing the cartridge to go dry at the end of the transfer. This eluate is also discarded.

4.0 Sample Elution from the SPE Cartridge:

4.1. Place a collection tube under the cartridge in the vacuum manifold in which to collect the sample extract.

4.2. Connect a methanol rinsed ENVI-Carb cartridge to each sample cartridge prior to elution.

4.3. Rinse the bottle with 4 ml of 0.1 % ammonia/methanol. Elute the analytes from the cartridge by pulling this solution through the transfer lines onto the cartridge at a rate of one drop/second.

4.4. Rinse the bottle with 4 ml of Acetic Acid/methanol. Elute the cartridge by pulling this solution through the transfer lines onto the cartridge at a rate of one drop/second.

4.5. Elute the cartridge with 2 mL of Methanol.

4.6. Allow the cartridge to go dry.

4.7. Reweigh the empty sample bottle with its original cap and calculate the net mass of sample, to the nearest 1 g, from the difference in weight. Assuming a density of 1 g/ml, the value of the net mass (in grams) is equivalent to the volume (in milliliters) of the water used in the extraction.

5.0 Concentration

5.1. Evaporate the eluate with a gentle stream of nitrogen gas at 50 ± 5 ºC to a final volume of 4 mL.

5.2. Adjust the final volume to 5 mL with 1 mL of reagent water for all liquids except drinking water. Adjust the final volume to 5 mL with 0.8 mL of methanol and 0.2 mL of water for drinking water.

6.0 Extract Preparation

6.1. Label an autosampler vial with each sample number including batch QC.

6.2. Add 200 uL of each extract to the vial.

6.3. Add 20 uL of Injection Internal standard to each vial.

APPENDIX 2: WATER EXTRACTION -CONTINUED

Note: For Drinking water samples, use 20 uL of the Extraction Internal Standard.

6.4. Cap the vial and vortex. The extract is now ready for analysis.

APPENDIX 3: SOLIDS EXTRACTION

1.0 Setup:

1.1. Perform daily calibration verification of the open top balance.
1.2. Homogenize the sample following procedure GL-LB-E-029.
1.3. Weigh 2.0 +/- 0.5g of sample in a 50 mL tube. Ottawa sand or prep analyzed fish tissue is used for the MB and LCS QC sample.
1.4. Add 250 µL of the ES standard to each sample and QC.
1.5. Add 500 µL of the spike intermediate standard to LCS, LCS DUP, matrix spike, and matrix spike DUP.
1.6. Add 5 mL (10 mL for tissue samples) of 0.1% Ammonia/Methanol to each vial.
1.7. Cap and gently shake to mix contents.
1.8. Shake the samples on a wrist action shaker for 30 minutes.
1.9. Remove the samples from the shaker and decant the liquid portion into a clean 50 mL tube.
1.10. Add 2.5 mL (5 mL for tissue samples) of 0.1% Ammonia/Methanol and return the sample to the shaker. Shake an additional 15 minutes.
1.11. Decant the sample into the 50 mL tube.
1.12. Repeat step 1.10 -1.11 once more.
1.13. Centrifuge the extract for 5 minutes.

Please note: The final volume for soil samples is 10 mL. The final volume for tissue is 20 mL.

2.0 ENVI-Carb Cartridge Conditioning:

2.1. Attach the ENVI-Carb SPE cartridge to the top of the manifold.
2.2. Fill the cartridge with 4 mL of methanol. Pull the solvent through the sorbent bed.
2.3. Dispose the discarded rinse solvents in the appropriate waste drum.

3.0 Sample Loading onto SPE Cartridge:

3.1. Place a collection tube under the cartridge in the vacuum manifold in which to collect the sample extract.
3.2. Add 5 mL of the centrifuged extract to the pre-rinsed cartridge.
3.3. Allow the sample to pass through the cartridge under the flow of gravity.
3.4. Rinse the cartridge with 4 mL of Acetic acid/methanol.
3.5. The sample is now ready for concentration.

APPENDIX 3: SOLIDS EXTRACTION-CONTINUED

4.0 Concentration

4.1. Evaporate the eluate with a gentle stream of nitrogen gas at 50 ± 5 ºC to a final volume of 4 mL.

4.2. Adjust the final volume to 5 mL with water.. The extract is now ready for analysis.

5.0 Extract Preparation

5.1. Label an autosampler vial with each sample number including batch QC.

5.2. Add 200 uL of each extract to the vial.

5.3. Add 20 uL of Injection Internal standard to each vial.

5.4. Cap the vial and vortex. The extract is now ready for analysis

APPENDIX 4: Aqueous Film Forming Foam (AFFF) Samples

1.0 Setup:

1.1. Weigh the sample container to the nearest 1 g.

1.2. Shake the container for several minutes, with the cap tightly sealed, to ensure that any particulate matter is evenly distributed.

1.3. Weigh out three separate aliquots of each sample (usually 0.5 - 1 mL) in HDPE containers. **Note: A sample duplicate (DUP) and matrix spike (MS) must be analyzed with each sample.**

1.4. Prepare a Method Blank (MB) and a Laboratory Control Sample (LCS) from a 1 mL volume of organic-free reagent water, or a volume of reagent water similar to that being used for the samples in HDPE containers.

1.5. Add 125 uL of a 10 ug/L ES Standard to the samples, the MB, LCS, and any Matrix Spikes associated to the extraction batch.

1.6. Add 250 uL of a 20 ug/L Spike intermediate standard to the LCS only.

1.7. Add 25 uL of a 20 ug/L Spike intermediate standard to the MS only. **Note: The MS must be spiked at the LOQ for all non-detected analytes.**

1.8. Add 3.875 mL of Methanol to the samples and method blank.

1.9. Add 3.625 mL of Methanol to the LCS and 3.850 mL of Methanol to the MS and MSD.

1.10. Cap the vial and vortex. The extract is now ready for analysis

2.0 Extract Preparation

2.1. Label an autosampler vial with each sample number including batch QC.

2.2. Add 200 uL of each extract to the vial.

2.3. Add 20 uL of Injection Internal standard to each vial.

2.4. Cap the vial and vortex. The extract is now ready for analysis.

APPENDIX 5: INITIAL DEMONSTRATION OF CAPABILITY QUALITY CONTROL REQUIREMENTS FOR DRINKING WATERS

Requirement	Specification and Frequency	Acceptance Criteria
Initial Demonstration of Low System Background	Analyze LRB prior to any other IDC steps.	All method analytes must be below 1/3 the MRL. Must also ensure that possible interferences from extraction media do not prevent the identification and quantification of method analytes.
Initial Demonstration of Precision (IDP)	Analyze four to seven replicate LFBs fortified near the midrange calibration concentration.	%RSD must be <20%
Initial Demonstration of Accuracy (IDA)	Calculate average recovery for replicates used in IDP.	Mean recovery ± 30% of true value
Initial Demonstration of Peak Asymmetry Factor	Calculate the peak asymmetry factor using the equation in Section 15.2.4 for the first two eluting chromatographic peaks in a mid-level CAL standard.	Peak asymmetry factor of 0.8 - 1.5
Minimum Reporting Limit (MRL) Confirmation	Fortify, extract and analyze seven replicate LFBs at the proposed MRL concentration. Calculate the Mean and the Half Range (HR). Confirm that the upper and lower limits for the Prediction Interval of Result (Upper PIR, and Lower PIR) meet the recovery criteria.	Upper PIR ≤150% Lower PIR ≥ 50%

APPENDIX 5: INITIAL DEMONSTRATION OF CAPABILITY QUALITY CONTROL REQUIREMENTS FOR DRINKING WATERS -CONTINUTED

Requirement	Specification and Frequency	Acceptance Criteria
Quality Control Sample (QCS)	Analyze a standard from a second source, as part of IDC.	Results must be within 70-130% of true value.
Detection Limit (DL) Determination (optional)	Over a period of three days, prepare a minimum of seven replicate LFBs fortified at a concentration estimated to be near the DL. Analyze the replicates through all steps of the analysis. Calculate the DL using the equation in Sect. 15.2.7	Data from DL replicates are not required to meet method precision and accuracy criteria. If the DL replicates are fortified at a low enough concentration, it is likely that they will not meet precision and accuracy criteria.

APPENDIX 6: ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY) FOR DRINKING WATERS

Requirement	Specification and Frequency	Acceptance Criteria
Sample Holding Time	14 days with appropriate preservation and storage as described in Section 11.0.	Sample results are valid only if samples are extracted within the sample holding time.
Extract Holding Time	28 days when stored at room temperature in centrifuge tubes.	Extract results are valid only if extracts are analyzed within the extract holding time.
Laboratory Reagent Blank (LRB)	With each extraction batch of up to 20 samples, whichever is more frequent.	Demonstrate that all method analytes are below 1/3 the MRL, and confirm that possible interferences do not prevent quantification of method analytes. If targets exceed 1/3 the MRL or if interferences are present, results for these analytes in the extraction batch are invalid.
Laboratory Fortified Blank (LFB)	Analyze at least one LFB daily or one for each extraction batch of up to 20 Field Samples. Rotate the fortified concentrations between low, medium and high amounts.	Results of LFB analyses must be 70-130% of the true value for each method analyte for all fortified concentrations except the lowest CAL point. Results of the LFBs corresponding to the lowest CAL point for each method analyte must be 50-150% of the true value.

APPENDIX 6: ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY) FOR DRINKING WATERS-CONTINUED

Requirement	Specification and Frequency	Acceptance Criteria
Internal Standard (IS)	Internal standards, $^{13}C_4$-PFBA, $^{13}C_5$-PFPeA, $^{13}C_3$-PFBS, $^{13}C_5$-PFHxA, $^{13}C_2$-4:2 FTS, $^{13}C_4$-PFHpA, $^{13}C_3$-PFHxS, $^{13}C_8$-PFOA, $^{13}C_2$-6:2 FTS, $^{13}C_9$-PFNA, $^{13}C_8$-PFOS, $^{13}C_8$-PFOSA, $^{13}C_6$-PFDA, $^{13}C_2$-8:2 FTS, $^{13}C_7$-PFUdA, d_3-NMeFOSAA, d_5-NEtFOSAA, $^{13}C_2$-PFDoA, and $^{13}C_2$-PFTeDA are added to all standards and sample extracts, including QC samples just prior to analysis. Compare IS areas to the average IS area in the initial calibration and to the most recent continuing calibration	Peak area counts for all ISs in all injections must be within ± 50% of the average peak area calculated during the initial calibration and 70-140% from the most recent CCV If ISs do not meet this criterion, corresponding target results are invalid.
Surrogate Standards	Surrogate standards, $^{13}C_2$-PFOA, $^{13}C_2$-PFDA, $^{13}C_4$-PFOS and $^{13}C_3$-PFBA, are added to all CAL standards and samples, including QC samples. Calculate the surrogate recoveries.	Surrogate recoveries must be 70-130% of the true value. If a SUR fails this criteria, report all results for sample as suspect/surrogate recovery.

APPENDIX 6: ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY) FOR DRINKING WATERS-CONTINUED

Requirement	Specification and Frequency	Acceptance Criteria
Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per extraction batch (20 samples or less) fortified with method analytes at a concentration close to but greater than the native concentration, if known. Calculate LFSM recoveries.	Recoveries at mid and high levels should be within 70-130% and within 50-150% at the low-level fortified amount (near the MRL). If these criteria are not met, results are labeled suspect due to matrix effects.
Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicates (FD)	Extract and analyze at least one FD or LFSMD with each extraction batch (20 samples or less). A LFSMD may be substituted for a FD when the frequency of detects are low. Calculate RPDs.	Method analyte RPDs for the LFMD or FD should be ≤30% at mid and high levels of fortification and ≤50% near the MRL. If these criteria are not met, results are labeled suspect due to matrix effects.
Field Reagent Blank (FRB)	Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the MRL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample.	If the method analyte(s) found in the Field Sample is present in the FRB at a concentration greater than 1/3 the MRL, then all samples collected with that FRB are invalid and must be recollected and reanalyzed.
Peak Asymmetry Factor	Calculate the peak asymmetry factor for the first two eluting chromatographic peaks in a mid-level CAL standard every time a calibration curve is generated.	Peak asymmetry factor of 0.8 - 1.5
Quality Control Sample (QCS)	Analyze at least quarterly or when preparing new standards, as well as during the IDC.	Results must be within 70-130% of true value.
Initial Calibration	Use IS calibration technique to generate a first or second order calibration curve forced through zero. Use at least five standard concentrations. Check the calibration curve as described in Sect. 17.4.	When each CAL standard is calculated as an unknown using the calibration curve, the analyte results should be 70-130% of the true value for all except the lowest standard, which should be 50-150% of the true value. Recalibration is recommended if these criteria are not met.

APPENDIX 6: ONGOING QUALITY CONTROL REQUIREMENTS (SUMMARY) FOR DRINKING WATERS-CONTINUED

Requirement	Specification and Frequency	Acceptance Criteria
Continuing Calibration Check (CCV)	Verify initial calibration by analyzing a low level (at the MRL or below) CCV prior to analyzing samples. CCVs are then injected after every 10 samples and after the last sample, rotating concentrations to cover the calibrated range of the instrument.	Recovery for each analyte and SUR must be within 70-130% of the true value for all but the lowest level of calibration. Recovery for each analyte in the lowest CAL level CCV must be within 50-150% of the true value and the surrogate must be within 70-130% of the true value.

APPENDIX 7: PFCS CALIBRATION CONCENTRATIONS FOR GROUNDWATER

Groundwater Calibration Chart	Level 1 (ng/L)	Level 2 (ng/L)	Level 3 (ng/L)	Level 4 (ng/L)	Level 5 (ng/L)	Level 6 (ng/L)	Level 7 (ng/L)	Level 8 (ng/L)	Level 9 (ng/L)
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	100	200	500	750	1000	1500	2000	5000	10000
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorobutyric acid (PFBA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorodecanoic acid (PFDA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorododecanoic acid (PFDoA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoroheptanoic acid (PFHpA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorohexanoic acid (PFHxA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoropentanoic acid (PFPeA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorononanoic acid (PFNA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctanesulfonamide (PFOSA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctanesulfonic acid (PFOS)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctanoic acid (PFOA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorotetradecanoic acid (PFTeDA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorotridecanoic acid (PFTrDA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoroundecanoic acid (PFUdA)	100	200	500	750	1000	1500	2000	5000	10000
Fluorotelomer sulfonate 4:2 (4:2 FTS)	93.5	187.0	467.5	701.3	935.0	1402.5	1870.0	4675	9350
Fluorotelomer sulfonate 6:2 (6:2 FTS)	95.0	190.0	475.0	712.5	950.0	1425.0	1900.0	4750	9500
Fluorotelomer sulfonate 8:2 (8:2 FTS)	96.0	192.0	480.0	720.0	960.0	1440.0	1920.0	4800	9600
Perfluorobutanesulfonate (PFBS)	88.5	177.0	442.5	663.8	885.0	1327.5	1770.0	4425	8850
Perfluorodecanesulfonate (PFDS)	96.5	193.0	482.5	723.8	965.0	1447.5	1930.0	4825	9650
Perfluoroheptanesulfonate (PFHpS)	95.0	190.0	475.0	712.5	950.0	1425.0	1900.0	4750	9500
Perfluorohexanesulfonate (PFHxS)	91.2	182.4	456.0	684.0	912.0	1368.0	1824.0	4560	9120
Perfluorononanesulfonate (PFNS)	96.0	192.0	480.0	720.0	960.0	1440.0	1920.0	4800	9600
Perfluoropentanesulfonate (PFPeS)	94.0	188.0	470.0	705.0	940.0	1410	1880.0	4700	9400
Perfluoro-2-propoxypropanoic Acid (GenX) (PFPrOPrA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro-2-methoxyacetic acid (PFMOAA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro-4-methoxybutanic acid (PFMOBA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	100	200	500	750	1000	1500	2000	5000	10000

Nafion Byproduct 1	100	200	500	750	1000	1500	2000	5000	10000
Nafion Byproduct 2	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctadecanoic acid (PFHODA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorohexadecanoic acid (PFHxDA)	100	200	500	750	1000	1500	2000	5000	10000
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	100	200	500	750	1000	1500	2000	5000	10000
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	100	200	500	750	1000	1500	2000	5000	10000
N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)	100	200	500	750	1000	1500	2000	5000	10000
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	100	200	500	750	1000	1500	2000	5000	10000
N-methylperfluoro-1-octanesulfonamide (N-MeFOSA)	100	200	500	750	1000	1500	2000	5000	10000
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (PF3ONS)	100	200	500	750	1000	1500	2000	5000	10000
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS)	100	200	500	750	1000	1500	2000	5000	10000
Sodium 2,2,4,4,6,6,8,8,10,10,12,12,12-tridecafluoro-3,5,7,9,11-pentaoxadodecanoate (TAF)	100	200	500	750	1000	1500	2000	5000	10000
4-(Heptafluoroisopropoxy)hexafluorobutanoic acid (PFECA-G)	100	200	500	750	1000	1500	2000	5000	10000
Fluorotelomer sulfonate 10:2 (10:2 FTS)	96.0	192.0	480.0	720.0	960.0	1440.0	1920.0	4800	9600
$^{13}C_2$PFHxDA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
d-N-EtFOSA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
d_9-N-EtFOSE (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
d_7-N-MeFOSE (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
d-N-MeFOSA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_3$-PFPrOPrA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250

$^{13}C_4$-PFHpA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_8$-PFOSA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
d_3-MeFOSAA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$_5$-EtFOSAA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-PFDoA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_8$-PFOS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_3$-PFBS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-4:2 FTS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_5$-PFHxA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_3$-PFHxS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-6:2 FTS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_8$-PFOA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_9$-PFNA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250

APPENDIX 7: PFCS CALIBRATION CONCENTRATIONS FOR GROUNDWATER- CONTINUED

$^{13}C_2$-8:2 FTS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_6$-PFDA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	
$^{13}C_7$-PFUdA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-PFTeDA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_4$-PFBA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_5$-PFPeA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_4$-PFOS (INJECTED INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_3$-PFBA (INJECTED INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-PFOA (INJECTED INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-PFDA (INJECTED INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-PFDoA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_8$-PFOS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_3$-PFBS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-4:2 FTS (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250
$^{13}C_5$-PFHxA (EXTRACTED INTERNAL STANDARD)	250	250	250	250	250	250	250	250	250

APPENDIX 8: PFCS CALIBRATION CONCENTRATIONS FOR DRINKING WATER

Drinking Water Calibration Chart	Level 1 (ng/L)	Level 2 (ng/L)	Level 3 (ng/L)	Level 4 (ng/L)	Level 5 (ng/L)	Level 6 (ng/L)	Level 7 (ng/L)	Level 8 (ng/L)	Level 9 (ng/L)
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	100	200	500	750	1000	1500	2000	5000	10000
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorobutyric acid (PFBA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorodecanoic acid (PFDA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorododecanoic acid (PFDoA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoroheptanoic acid (PFHpA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorohexanoic acid (PFHxA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoropentanoic acid (PFPeA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorononanoic acid (PFNA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctanesulfonamide (PFOSA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctanesulfonic acid (PFOS)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctanoic acid (PFOA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorotetradecanoic acid (PFTeDA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorotridecanoic acid (PFTrDA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoroundecanoic acid (PFUdA)	100	200	500	750	1000	1500	2000	5000	10000
Fluorotelomer sulfonate 4:2 (4:2 FTS)	93.5	187.0	467.5	701.3	935.0	1402.5	1870	4675	9350
Fluorotelomer sulfonate 6:2 (6:2 FTS)	95.0	190.0	475.0	712.5	950.0	1425.0	1900	4750	9500
Fluorotelomer sulfonate 8:2 (8:2 FTS)	96.0	192.0	480.0	720.0	960.0	1440.0	1920	4800	9600
Perfluorobutanesulfonate (PFBS)	88.5	177.0	442.5	663.8	885.0	1327.5	1770	4425	8850
Perfluorodecanesulfonate (PFDS)	96.5	193.0	482.5	723.8	965.0	1447.5	1930	4825	9650
Perfluoroheptanesulfonate (PFHpS)	95.0	190.0	475.0	712.5	950.0	1425.0	1900	4750	9500
Perfluorohexanesulfonate (PFHxS)	91.2	182.4	456.0	684.0	912.0	1368.0	1824	4560	9120
Perfluorononanesulfonate (PFNS)	96.0	192.0	480.0	720.0	960.0	1440.0	1920	4800	9600
Perfluoropentanesulfonate (PFPeS)	94.0	188.0	470.0	705.0	940.0	1410.0	1880	4700	9400
Perfluoro-2-propoxypropanoic Acid (GenX) (PFPrOPrA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro-2-methoxyacetic acid (PFMOAA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro-4-methoxybutanic acid (PFMOBA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	100	200	500	750	1000	1500	2000	5000	10000
Nafion Byproduct 1	100	200	500	750	1000	1500	2000	5000	10000

Nafion Byproduct 2	100	200	500	750	1000	1500	2000	5000	10000
Perfluorooctadecanoic acid (PFHODA)	100	200	500	750	1000	1500	2000	5000	10000
Perfluorohexadecanoic acid (PFHxDA)	100	200	500	750	1000	1500	2000	5000	10000
Sodium dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	100	200	500	750	1000	1500	2000	5000	10000
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)	100	200	500	750	1000	1500	2000	5000	10000
N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)	100	200	500	750	1000	1500	2000	5000	10000

APPENDIX 8: PFCS CALIBRATION CONCENTRATIONS FOR DRINKING WATER-CONTINUED

Drinking Water Calibration Chart	Level 1 (ng/L)	Level 2 (ng/L)	Level 3 (ng/L)	Level 4 (ng/L)	Level 5 (ng/L)	Level 6 (ng/L)	Level 7 (ng/L)	Level 8 (ng/L)	
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)	100	200	500	750	1000	1500	2000	5000	10000
N-methylperfluoro-1-octanesulfonamide (N-MeFOSA)	100	200	500	750	1000	1500	2000	5000	10000
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (PF3ONS)	100	200	500	750	1000	1500	2000	5000	10000
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (PF3OUdS)	100	200	500	750	1000	1500	2000	5000	10000
Sodium 2,2,4,4,6,6,8,8,10,10,12,12,12-tridecafluoro-3,5,7,9,11-pentaoxadodecanoate (TAF)	100	200	500	750	1000	1500	2000	5000	10000
4-(Heptafluoroisopropoxy)hexafluorobutanoic acid (PFECA-G)	100	200	500	750	1000	1500	2000	5000	10000
Fluorotelomer sulfonate 10:2 (10:2 FTS)	96.0	192.0	480.0	720.0	960.0	1440.0	1920.0	4800	9600
$^{13}C_2$PFHxDA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
d-N-EtFOSA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
d_9-N-EtFOSE (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
d_7-N-MeFOSE (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
d-N-MeFOSA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_3$-PFPrOPrA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_4$-PFHpA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_8$-PFOSA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
d_3-MeFOSAA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000

d_5-EtFOSAA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-PFDoA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_8$-PFOS (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_3$-PFBS (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-4:2 FTS (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_5$-PFHxA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_3$-PFHxS (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-6:2 FTS (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000

APPENDIX 8: PFCS CALIBRATION CONCENTRATIONS FOR DRINKING WATER-CONTINUED

Drinking Water Calibration Chart	Level 1 (ng/L)	Level 2 (ng/L)	Level 3 (ng/L)	Level 4 (ng/L)	Level 5 (ng/L)	Level 6 (ng/L)	Level 7 (ng/L)	Level 8 (ng/L)	
$^{13}C_8$-PFOA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_9$-PFNA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-8:2 FTS (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_6$-PFDA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_7$-PFUdA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_2$-PFTeDA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_4$-PFBA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_5$-PFPeA (INTERNAL STANDARD)	1000	1000	1000	1000	1000	1000	1000	1000	1000
$^{13}C_4$-PFOS (SURROGATE)	250	250	250	250	250	250	250	250	250
$^{13}C_3$-PFBA (SURROGATE)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-PFOA (SURROGATE)	250	250	250	250	250	250	250	250	250
$^{13}C_2$-PFDA (SURROGATE)	250	250	250	250	250	250	250	250	250

APPENDIX 9: WASTER WATER EXTRACTION

Waste Water Extraction

Preservative Type

_____ (4°C) no preservative

- **May contain Trizma**

Condition Cartridge

_____ 4 mL 0.1% ammonia in MeOH
_____ 4 mL methanol
_____ 4 mL water

Surrogate and Spike

_____ All samples (125 uL of **IS**)

_____ LCS, MS, MSD (250 uL **PFAS** Spike)

Rinse Samples

_____ 4 mL water (wet)
_____ 4 mL acetate buffer (dry)

Elute Samples

_____ Stack preconditioned cartridge (4 mL MeOH)

_____ 4 mL 0.1% ammonia in MeOH (wet)
_____ 4 mL methanol (dry)

Final Volume

_____ Concentrate sample to Approximately 4 mL
_____ Add 0.2 mL of water
_____ Adjust final volume to 5 mL with methanol

APPENDIX 10: DRINKING WATER EXTRACTION

Drinking Water Extraction

The Extraction of Per and Polyfluroalkyl Substances

Preservative Type

_____ Trizma - 1.25g for MB, LCS, LCSD

Condition Cartridge

_____ 4 mL 0.1% ammonia in MeOH
_____ 4 mL methanol
_____ 4 mL water

Add Surrogate

_____ All samples (125 uL of **IS**)

Add Spike

_____ LCS, MS, MSD (250 uL **PFAS** Spike)

Rinse Samples

_____ 4 mL water (wet)
_____ 4 mL acetate buffer (dry)

Elute Samples

_____ 4 mL 0.1% ammonia in MeOH (wet)
_____ 4 mL methanol (dry)

Final Volume

_____ Concentrate sample to Approximately 4 mL
_____ Add 0.2 mL of water
_____ Adjust final volume to 5 mL with methanol

TABLE 1. ANALYTE LIST

Compound	Acronym	CAS Number
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorobutyric acid	PFBA	375-22-4
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUdA	2058-94-8
Fluorotelomer sulfonate 4:2	4:2 FTS	757124-72-4
Fluorotelomer sulfonate 6:2	6:2 FTS	27619-97-2
Fluorotelomer sulfonate 8:2	8:2 FTS	39108-34-4
Perfluorobutanesulfonate	PFBS	375-73-5
Perfluorodecanesulfonate	PFDS	335-77-3
Perfluoroheptanesulfonate	PFHpS	375-92-8
Perfluorohexanesulfonate	PFHxS	355-46-4
Perfluorononanesulfonate	PFNS	68259-12-1
Perfluorooctanesulfonamide	PFOSA	754-91-6
Perfluoropentanesulfonate	PFPeS	2706-91-4
Perfluoro-2-propoxypropanoic Acid (GenX)	PFPrOPrA	13252-13-6
Perfluorooctadecanoic acid	PFODA	16517-11-6
Perfluorohexadecanoic acid	PFHxDA	67905-19-5

TABLE 1. ANALYTE LIST- CONTINUED

Compound	Acronym	CAS Number
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	N-EtFOSE	1691-99-2
N-ethylperfluoro-1-octanesulfonamide	N-EtFOSA	4151-50-2
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	N-MeFOSE	24448-09-7
N-methylperfluoro-1-octanesulfonamide	N-MeFOSA	31506-32-8
Perfluoro-2-methoxyacetic acid	PFMOAA	674-13-5
Perfluoro-3-methoxypropanoic acid	PFMOPrA	377-73-1
Perfluoro-4-methoxybutanic acid	PFMOBA	863090-89-5
Perfluoro(3,5-dioxahexanoic) acid	PFO2HxA	39492-88-1
Perfluoro(3,5,7-trioxaoctanoic) acid	PFO3OA	39492-89-2
Perfluoro(3,5,7,9-tetraoxadecanoic) acid	PFO4DA	39492-90-5
Nafion Byproduct 1	NAFION_BP1	29311-67-9
Nafion Byproduct 2	NAFION_BP2	749836-20-2
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	PF3ONS	73606-19-6
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	PF3OUdS	83329-89-9
Sodium 2,2,4,4,6,6,8,8,10,10,12,12,12-tridecafluoro-3,5,7,9,11-pentaoxadodecanoate	TAF	39492-91-6
4-(Heptafluoroisopropoxy)hexafluorobutanoic acid	PFECA-G	801212-59-9
Fluorotelomer sulfonate 10:2	10:2 FTS	120226-60-0

TABLE 2. MS/MS METHOD CONDITIONS

Analyte	Precursor Ion (*m/z*)	Product Ion (*m/z*)
PFBA	212.9	169
PFPeA	262.9	219
PFBS	298.9	80
PFHxA	313	269
4:2 FTS	327	307
PFHpA	363	319
PFPeS	349	80
PFHxS	399	80
PFOA	413	369
6:2 FTS	427	407
PFHpS	449	80
PFNA	463	419
PFOSA	498	78
PFOS	499	80
PFDA	513	469
8:2 FTS	527	507
PFNS	549	80
PFUdA	563	519
N-MeFOSAA	570	419
NEtFOSAA	584	419
PFDS	599	80
PFDoA	613	569
PFTrDA	663	619
PFTeDA	713	219
PFPrOPrA	329	185
PFODA	913	869
PFHxDA	813	769
N-EtFOSA	526	169

TABLE 2. MS/MS METHOD CONDITIONS- CONTINUED

Analyte	Precursor Ion (*m/z*)	Product Ion (*m/z*)
N-EtFOSE	630	59
N-MeFOSA	512	169
N-MeFOSE	616	59
ADONA	377	251
PFMOAA	179	85
PFMOPrA	229	185
PFMOBA	279	235
PFO2HxA	245	85
PFO3OA	311	85
PFO4DA	377	85
NAFION BP_1	442.9	147
NAFION BP_2	462.9	185
PF3ONS	530.9	351
PF3OUdS	631.1	451
TAF	442.9	85
PFECA_G	378.9	184.9
10:2 FTS	626.8	606.9
$^{13}C_4$-PFHpA	367	322
$^{13}C_4$-PFOS	503	80
$^{13}C_8$-PFOSA	506	78
$^{13}C_2$-PFDA	515	470
d_3-MeFOSAA	573	419
d_5-EtFOSAA	589	419
$^{13}C_2$-PFDoA	615	570
$^{13}C_3$-PFBA	216	172
$^{13}C_2$-PFOA	415	370
$^{13}C_8$-PFOS	507	99

$^{13}C_3$-PFBS	302	99
$^{13}C_2$-4:2 FTS	329	81
$^{13}C_5$-PFHxA	318	273
$^{13}C_3$-PFHxS	402	99
$^{13}C_2$-6:2 FTS	429	81
$^{13}C_8$-PFOA	421	376
$^{13}C_9$-PFNA	472	427
$^{13}C_2$-8:2 FTS	529	81
$^{13}C_6$-PFDA	519	474

TABLE 2. MS/MS METHOD CONDITIONS- CONTINUED

Analyte	Precursor Ion (*m/z*)	Product Ion (*m/z*)
$^{13}C_7$-PFUdA	570	525
$^{13}C_2$-PFTeDA	715	670
$^{13}C_4$-PFBA	217	172
$^{13}C_5$-PFPeA	267.9	223
$^{13}C_2$PFHxDA	815	770
d-N-EtFOSA	531	169
d_9-N-EtFOSE	639	59
d_7-N-MeFOSE	623	59
d-N-MeFOSA	515	169
$^{13}C_3$-PFPrOPrA	332	169

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STANDARD OPERATING PROCEDURE

MT 007 Acid Digestion of Solids and Semi-solids for Total Metals by GFAA and ICP

Review Date: 05/29/2019

05/29/2019

Technical Review by: Date

05/29/2019

Approved by: Quality Assurance Date

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1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare soils, sediments, sludges, oils, paint chips, tissue samples, wipes and other solid waste samples for analysis by ICP, FLAA, or GFAA spectroscopy for the following metals:

Aluminum*	Calcium*	Magnesium*	Silver*
Antimony*	Chromium	Manganese*	Sodium*
Arsenic	Cobalt	Molybdenum	Strontium*
Barium*	Copper*	Nickel *	Thallium
Beryllium	Iron	Potassium*	Vanadium*
Cadmium	Lead	Selenium	Zinc*

* Cannot be used for GFAA for selected element

1.2 For analysis by ICP or FLAA both HCl and HNO_3 are used in the digestion procedure. For analysis by GFAA, HNO_3 only is used.

2.0 METHOD SUMMARY

2.1 For the digestion of samples, a representative 0.5 gram sample or 1-2g for QSM soil or 4g for tissue samples for QSM work is digested with repeated additions of nitric acid and hydrogen peroxide

2.2 For GFAA analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 50 ml.

2.3 For ICP (trace) or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. The digestate is then diluted to a final volume of 50 ml.

3.0 DEFINITIONS

3.1 Batch - A batch consists of a maximum of 20 samples of similar matrix which are prepared and analyzed in the same manner. Each batch is given a unique prep batch number for tracking purposes.

3.2 Reagent Blank **-** A solution of de-ionized water, (containing in correct proportion, all reagents required by the method), used with the calibration standards to standardize the instrument, as a calibration blank, and for sample dilution.

3.3 LCS (Laboratory Control Sample) - A mid-range standard prepared from a source different from that used for calibration standards. The LCS is used to verify the accuracy of the digestion procedure and is analyzed at the beginning of the analytical batch.

3.4 MB (Method Blank) - A reagent blank which is carried through the entire preparation and analytical method. The method blank is used to detect possible contamination that may occur prior to or during the sample preparation process. A minimum of one MB is prepared per batch and is analyzed at the beginning of an analytical batch.

3.5 MS-MSD (Matrix Spike-Matrix Spike Duplicate): - Two separate sample aliquots to which a known concentration of analyte has been added which is carried through the entire preparation and analytical procedure. The purpose of a matrix spike is to reveal any matrix effect from the sample on the recovery of the analyte by the method being used. An MS-MSD pair is prepared for every batch (see 3.1) of routine samples. An MS and a DUP are prepared for every ACOE batch. Failure to meet criteria may be due to poor recovery during the preparation method or to matrix interference within the digestate. To be considered acceptable, MSD's must meet both the same % recovery criteria as an MS, and the same % RPD as a duplicate sample. MS/MSD %RPD may be used as acceptance criteria for duplicate analysis.

3.6 Duplicate (DUP) - A separate aliquot of sample which has been carried through the entire preparation and analytical procedure the same as the original sample. One duplicate per batch is prepared for ACOE work.

4.0 HEALTH AND SAFETY

4.1 Gloves, protective eyewear, and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

5.0 CAUTIONS

5.1 The extracts from GFAA and FLAA/ICP are not interchangeable and should only be used with the analytical determinations outlined.

5.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

5.3 Reagent grade chemicals shall be used in all tests. The reagent blank must be less than the MDL in order to be used.

6.0 INTERFERENCES

6.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality

control requirements to aid in determining whether Method 3050B is applicable to a given waste.

7.0 PERSONNEL QUALIFICATIONS

7.1 All personnel performing this analysis shall be instructed in the use of personal protective equipment prior to beginning analysis.

7.2 Personnel shall know how to read a meniscus and how to use a pipette correctly.

8.0 APPARATUS AND MATERIALS

8.1 Equipment Required

8.1.1 Thomas Cain DEENA Automated Sample Preparation Systems with reflux trays (DEENA I and DEENA II or equivalent)

8.1.2 Environmental Express Hotblock Digestion Apparatus: To maintain a temperature of 90-95°C.

8.1.3 50 mL Class A plastic hotblock digestion tubes, with watch glasses and storage caps. (Environmental Express p/n SC475 and SC505 or equivalent)

8.1.4 Qualitative filter paper and filter funnels.

8.1.5 Filtermate Teflon digestion tube filters: (Environmental Express p/n SC0401 or equivalent)

8.1.6 Teflon boiling stone/beads (Chemware, Item # 0919120 or equivalent)

8.1.7 GF Syringe Filter (Part# SFGF025100MCU or equivalent)

8.1.8 Thermometer: For monitoring temperature of the block at beginning and end of digestion process.

8.1.9 Balance: 0.01g capacity.

8.2 REAGENTS

8.2.1 ASTM Type II Water (ASTM D1193): Water should be monitored for impurities.

8.2.2 Concentrated Nitric Acid, trace metals grade (HNO_3): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to identify potential contamination problems. If contamination is

detected at any point and the problem is limited to a given bottle, the acid may be replaced with another bottle from the same lot. If the entire lot is a problem, then any remaining acid from the contaminated lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained. All acid used to make standards is recorded in the log book when the standard is made.

8.2.3 Concentrated Hydrochloric Acid, trace metals grade (HCl): Acid is of sufficient purity and comes with a certificate of analysis. All metals levels are lower than our lowest detection limits for any given element. However, each acid lot is logged in and tracked to each individual bottle to identify potential contamination problems. If contamination is detected at any point and the problem is limited to a given bottle, the acid may be replaced with another bottle from the same lot. If the entire lot is a problem, then any remaining acid from the contaminated lot will be removed from the lab and a replacement acid from a different lot of sufficient purity shall be obtained. All acid used to make standards is recorded in the log book when the standard is made.

8.2.4 Hydrogen Peroxide, 30% (H_2O_2): Each peroxide lot is logged in and tracked to each individual bottle to identify potential contamination problems. If contamination is detected at any point and the problem is limited to a given bottle, the peroxide may be replaced with another bottle from the same lot. If the entire lot is a problem, then any remaining peroxide from the contaminated lot will be removed from the lab and a replacement hydrogen peroxide bottle from a different lot shall be obtained.

8.2.5 SPEX Certiprep Spike- SPEX catalog number SPIKE 1-500

8.2.6 Molybdenum- 1,000 mg/L standard SPEX PLMO9-2Y or equivalent

8.2.7 Potassium-10,000 mg/L standard PLK2-3X or equivalent

8.2.8 Ultra Custom Standard – Ultra Catalog number ICUS192 or equivalent

8.2.9 Inorganic Venture Spike- Inorganic Venture catalog number SPK1 or equivalent

9.0 INSTRUMENT OR METHOD CALIBRATION

9.1 *DEENA Calibration:*

9.1.1 Prior to digesting any samples using the automated sample digester, the system needs to be calibrated.

9.1.2 After logging into the DEENA system (refer to sections 11.2.2-11.2.5), click on the “manual mode” tab at the top of the screen.

9.1.3 Click the “pump calibration” tab (figure 4).

9.1.4 Weigh out 5 digestion tubes and record their weights in the “initial weight” column for the 5 tubes.

9.1.5 Click “Go All”. The digester is dispensing water into the 5 empty tubes.

9.1.6 The tubes are then weighed again and the final weight is recorded in the “final weight” column.

9.1.7 The difference between the final weight and the initial weight is the amount of volume dispensed per “X” steps on the peristaltic pump. An average is then taken between the 5 replicates. The digester is now calibrated.

9.2 *Hot Block Calibration:*

9.2.1 Please refer to the Hot Block operator manual for instrument temperature calibration.

10.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

10.1 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. Note: Environmental Express provides a certificate of analysis with each tube lot.

10.2 Samples shall be refrigerated upon receipt and analyzed within 180 days.

11.0 SAMPLE PREPARATION AND ANALYSIS

11.1 *Manual Digestion:*

11.1.1 Turn on hot blocks to allow them to warm up. The switch is located on the right outer side of hood. Place a thermometer into a centrifuge tube of water and place it in the hot block to monitor the temperature of the hot block to insure the temperature is acceptable prior to use. The temperature should be 95 $\pm$ 5°C for digestion.

11.1.2 Carefully weigh on a balance and then transfer a 0.5 g representative portion (for routine work) or for QSM work 1-2g randomly or for tissue samples 4 g* of the sample to a tube, or use a known volume of a sludge sample based on the viscosity of the sample. Do not use metal spatulas. Refer to the subsampling SOP PR007 for instructions

on subsampling from the original sample. For some samples it is acceptable to use a larger sample size following the guidelines below:

Wet solids:	Up to 1.0 g.
Wipes:	The entire wipe is used.
Biological tissue:	Up to 2.0 g.
"liquidy" sludges	Up to 2.0 g
*Tissue samples	Typically 4.0 g sample since the tissue homogenization only yields 2.0g of sample when Milli Q DI H2O is added @ a 1:1 ratio during preparation.

11.1.2.1 Teflon boiling stone/beads (Chemware, Item # 0919120 or equivalent) are used as the solids matrix match for MB and LCS preparation. Weigh the appropriate amount and add to the digestion tube prior to digestion.

11.1.3 For samples to be spiked (MS, MSD, LCS), add the appropriate amount of spiking solution to sample (see Pre-digestion Spikes-LCS & LFB chart attached).

11.1.4 Add 5 mL 1:1 HNO_3 to routine samples or 10mL of 1:1 HNO_3 for ACOE samples, mix, and cover the tube with a watch glass. Do not handle the underside of the watch glass at any time, in order to prevent contamination. Place the tubes in the hotblock and heat the samples until they reflux for 10-15 minutes. For wipe samples, add DI water to wet the entire wipe if needed.

11.1.5 Add 2.5 mL concentrated HNO_3 to all routine samples and 5mL of concentrated HNO_3 to ACOE samples.

11.1.6 Place thermometer in one block location, record temperature in the sample prep book for the initial block temperature recording. Record again at the end of the digestion process in a different spot on the block. Rotate the placement of the thermometer between digestion batches to ensure that no "hot spots" develop on the block.

11.1.7 Return to the hotblock, and reflux the samples for 30 minutes. Do not allow the samples to go dry. If samples are still generating "brown" fumes, continue to add concentrated HNO_3 in 5mL increments until no more "brown" fumes are generated.

11.1.8 Allow the solution to evaporate to 5 mL without boiling or heat at 95°C ± 5°C without boiling for 2 hours. Do not allow samples to go to dryness.

11.1.9 Remove the samples from the hotblock and let cool to avoid excessive effervescence of hydrogen peroxide. For routine samples add 1 mL of DI water and 1.5 mL of 30% hydrogen peroxide to each tube. For DoD samples add 2 mL of DI water and 3 mL of 30% hydrogen peroxide to each tube (omit this step for Tin). Return to hot block and heat gently until the effervescence subsides.

11.1.10 Repeat step 11.9 two times or until effervescence is minimal for routine samples using a maximum of 5mL of 30% hydrogen peroxide. For ACOE samples, add 30% hydrogen peroxide in 1mL increments, up to 10mL, until the sample effervescence is minimized or the sample consistency is unchanged. It will not be necessary to cool down the samples between additions if they do not react too strongly.

11.1.11 Return samples to hot block and heat until volume is reduced to 2.5mL or heat at 95^0C ± 5°C without boiling for 2 hours.

11.1.12 For samples to be analyzed by ICP or FLAA, add 5 mL concentrated HCl for routine samples or for ACOE samples add 10mL of concentrated HCl and reflux for an additional 15 minutes. Omit this step for samples to be analyzed by GFAA.

11.1.13 Remove each tube from block using the tube racks provided and allow them to cool. Dilute to exactly 50 mL using the guide on the digestion tube and let sample sit to allow solids to settle out. If solids do not settle readily and remain suspended throughout sample, then it will be necessary to filter prior to analysis. Using the Environmental Express tube filters, push the filter down through the sample till it sits on the bottom. The digestion tubes are calibrated to 50mL ± 0.2mL.

11.1.14 Cap sample, taking care not to touch underside of cap or inside of container. To minimize contamination and for safety purposes appropriate gloves must be worn at any point where sample solution is being transferred. If gloves become stained and dirty, discard and replace, as the surface of the gloves themselves may also transfer contaminants.

11.1.15 If the digestate is clear and without solids distributed throughout the liquid portion, sample aliquots may be decanted for analysis. If not, then filtration will be necessary prior to analysis. Rinse a syringe filter (GF Syringe Filter, Part# SFGF025100MCU) with 2-3

ml of 10% HNO3 followed by 2-3 ml of DI H2O before filtering digestate.

11.2 *Automated Digestion (DEENA)*

11.2.1 See section 11.1.2-11.1.3 for weighing of samples.

11.2.2 Log-in to the computer associated to the DEENA automated sample preparation system.

11.2.3 Double-click on the DEENA shortcut icon on the desktop.

11.2.4 Next to “instrument selection”, select the sampler to be used. The program will open.

11.2.5 The blue light on the DEENA system will turn off, indicating that the computer is communicating with the instrument.

11.2.6 Prior to digesting samples, the automated digester needs to be calibrated. This is done before the first run of the day. See section 9.

11.2.7 Open up a template workspace. Click “file”, “new from”, “C-drive”, “program files”, “Thomas Cain”, “DEENA”. Choose the desired template for the method to be run.

11.2.8 Click the “automated mode” tab. The template that was chosen from the DEENA file is now loaded. The template will display the method steps, reagent list and tray setup.

11.2.9 Open the “method tab” and click the method to be run. Then click “ok”.

11.2.10 Click the “rack definition” tab. In the window, make sure start position is “1” and then fill in the number of samples to be digested. Click “ok” (figure 6).

11.2.11 Place the samples in the digestion block. Cover samples with reflux tray. Check to make sure all reagent bottles are at adequate volume for analysis. Click “run” on the screen.

11.2.12 Upon completion, save the workspace run log to Q-drive, DEENA I and II, run log by the date followed by rl1 or rl2 (designating a run log which instrument was used).

11.2.13 Remove digestion tubes from the system. Make sure final sample volume is accurate. Cap the digestion tubes. The samples are ready for analysis.

11.2.14 If the digestate is clear and without solids distributed throughout the liquid portion, sample aliquots may be decanted for analysis. If not, then filtration will be necessary prior to analysis. Rinse a syringe filter (GF Syringe Filter, Part# SFGF025100MCU) with 2-3 ml of 10% HNO3 followed by 2-3 ml of DI H2O before filtering digestate.

11.2.15 For detailed instructions for automated digestion, see the DEENA operator's manual, rev.1.2.3.

12.0 TROUBLESHOOTING

12.1 If method blank is higher than MDL, identify source of contamination. Contamination can come from many sources including the reagents used in the procedure and samples that were digested in the batch.

12.2 Over time, hot blocks can develop "hot spots". Monitor the temperature in different block spaces ensure that temperature is consistent throughout the hot block unit.

13.0 DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

There are no calculations for this method.

14.0 COMPUTER HARDWARE AND SOFTWARE

Computer with StarLIMS

15.0 DATA MANAGEMENT AND RECORD MANAGEMENT

15.1 Batch data information is recorded in the Digestion Log book.

15.2 Prep data is entered into LIMS, and then the batch sheet is given to the metals analyst.

16.0 QUALITY CONTROL

16.1 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation procedure.

16.2 By matrix, prepare one MS/MSD for routine work or one MS/DUP for ACOE work per 20 or fewer samples per matrix per digestion batch.

16.3 Prepare one LCS (lab control sample) for each digestion batch. The LCS source is carried through the entire digestion procedure. Prepare one LCS for every 20 samples per medium per day.

17.0 REFERENCES

17.1 *Test Methods for Evaluating Solid Waste*. USEPA SW-846, Rev 2 Dec 1996, Method 3050B.

17.0 CT Laboratories Quality Manual, current revision.

17.1 Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.

17.2 Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.1, January 2017 or most recent revision.

17.3 National Environmental Laboratory Accreditation Conference (NELAC), 2003 NELAC Standard Chapters 1 to 6, EPA/600/R-04/003, June 5, 2003 or most recent version.

17.4 ISO. 2005. General requirements for the competence of testing and calibration laboratories. ISO17025.

17.5 Thomas Cain, DEENA Operation Manual, Revision 1.2.3, November 2015

18.0 FIGURES

Figure 1: ICP/FLAA Table

SPIKE, & LFB ANALYSIS- ICP/FLAA Pre-digestion Spikes-LCS & LFB					
Element	**Spike Amt. mL**	**Spike Stock**	**Stock Conc. Mg/L**	**Final Vol mL**	**Expected Conc. Ug/L**
Aluminum	1	**A**	200	50	4000
Antimony	1	**A**	50	50	1000
Arsenic	1	**A**	200	50	4000
Barium	1	**A**	200	50	4000
Beryllium	1	**A**	5	50	100
Cadmium	1	**A**	5	50	100
Calcium	0.5	**C**	20,000	50	200000
Chromium	1	**A**	20	50	400
Cobalt	1	**A**	50	50	1000
Copper	1	**A**	25	50	500
Iron	1	**A**	100	50	2000
Lead	1	**A**	50	50	1000
Manganese	1	**A**	50	50	1000
Magnesium	0.5	**C**	10,000	50	100000
Molybdenum	0.1	**B**	1000	50	2000
Nickel	1	**A**	50	50	1000
Potassium	0.5	**D**	10,000	50	100000
Selenium	1	**A**	200	50	4000
Silver	1	**A**	5	50	100
Sodium	0.5	**C**	10,000	50	100000
Thallium	1	**A**	200	50	4000
Vanadium	1	**A**	50	50	1000
Zinc	1	**A**	50	50	1000

Spike Solutions		
Supplier	**Lot #/ std.**	**Stock**
SPEX Certiprep	SPIKE 1-500	**A**
Molybdenum	1000 mg/L	**B**
Ultra	ICUS 192	**C**
Potassium	10,000	**D**

Pre-Digestion Matrix Spike Prep for (GFAA)					
Element	**Spike Amt. mL**	**Spike Stock**	**Stock Conc. Mg/L**	**Final Vol mL**	**Expected Conc. Ug/L**
Antimony-GFAA	1.0	**A**	1000.0	50.0	20.0
Arsenic-GFAA	1.0	**A**	1000.0	50.0	20.0
Lead-GFAA	1.0	**A**	1000.0	50.0	20.0
Selenium-GFAA	1.0	**A**	1000.0	50.0	20.0
Thallium-GFAA	1.0	**A**	1000.0	50.0	20.0

Standard Source		
Supplier	**Dilution**	**Solution**
Inorg. Vent.-SPK1 (multi-element std.)	1/100	**A**

Figure 2: Metals Digestion Summary (FMT7-01, Example)

Analyst:		Metals Digestion Summary-CT Laboratories Baraboo								Date:	
Prep Batch#	Sample ID#	Matrix*	Prep Method**	Sample Amt gms or mls	Final Volume, mLs	Blk	Dup	MS	MSD	Spike/LCS/ LFB info	Acid ID#
Method Temperature Verification					*So,Sl,ww,gw,fish,tclp,splp,other					Review date/initials	
Block Used:		Initial Block Temp (C):			**3005,3010,3020,3050,3060					Digestion Tube Lot #:	
Cell #		Final Block Temp (C):			Comments:						

Figure 3: Metals Digestion Bench Sheet (FMT 3,4,5,6,7,8-01, Example)

FORM #: FMT3,4,5,6,7,8-01
Rev. #: 1.0
Effective Date: 05/17/2014

FMT3,4,5,6,7,8-01

Metals Digestion Bench Sheet

(Prep Methods 3010, 3020, 3005, & 3050)

Program: _____
*Matrix: _____

3010= ICP Liquids
3020= GFAA Liquids
3005= Sb Liquids
3050= ICP/GFAA Solids
7060/7740= GFAA, As & Se Liquids

Prep Batch #:	
Prep Method:	
Analyst:	
Date:	
Start Time:	

Prep Analyst: _____
Balance ID: _____

End Date: _____
End Time: _____
Digestion Tube Lot #: _____
Block Used: _____
Cell Position for Temp. Check: _____
Initial-DigestionTemp (°C): _____
Final-Digestion Temp (°C): _____

Reagent:	Ref. #
Nitric Acid:	
Hydrochloric Acid:	
Hydrogen Peroxide:	

Sample ID		(Solids) Sample Weight (g)	(Liquids) Sample Volume (ml)	Final Volume (ml)
	(MB)			50
	(LCS)			50
				50
	Comments:			50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
				50
	(DUP)			50
	(MS) Parent Sample			50
	(MSD)			50
Leave >>	(DUP) if applicable			50
blank	(MS) Parent Sample			50
if N/A	(MSD)			50

MB=Method Blank, LCS=Laboratory Control Sample, DUP=Duplicate, MS=Matrix Spike & MSD=Matrix Spike Duplicate
*Matrix: Soil, Sludge, Waste, GW=Groundwater, WW=Wastewater, Tissue, TLCP, SPLP, ASTM or other.

MS/MSD Spike Amount (ml)	Spike Ref. #

LCS Spike Amount (ml)	Spike Ref. #

Reviewed By/Date: _____

Page 1 of 1 Metals Prep Template_FMT3,4,5,6,7,8-01 03/25/1522:55

Figure 4: Calibration Window for DEENA

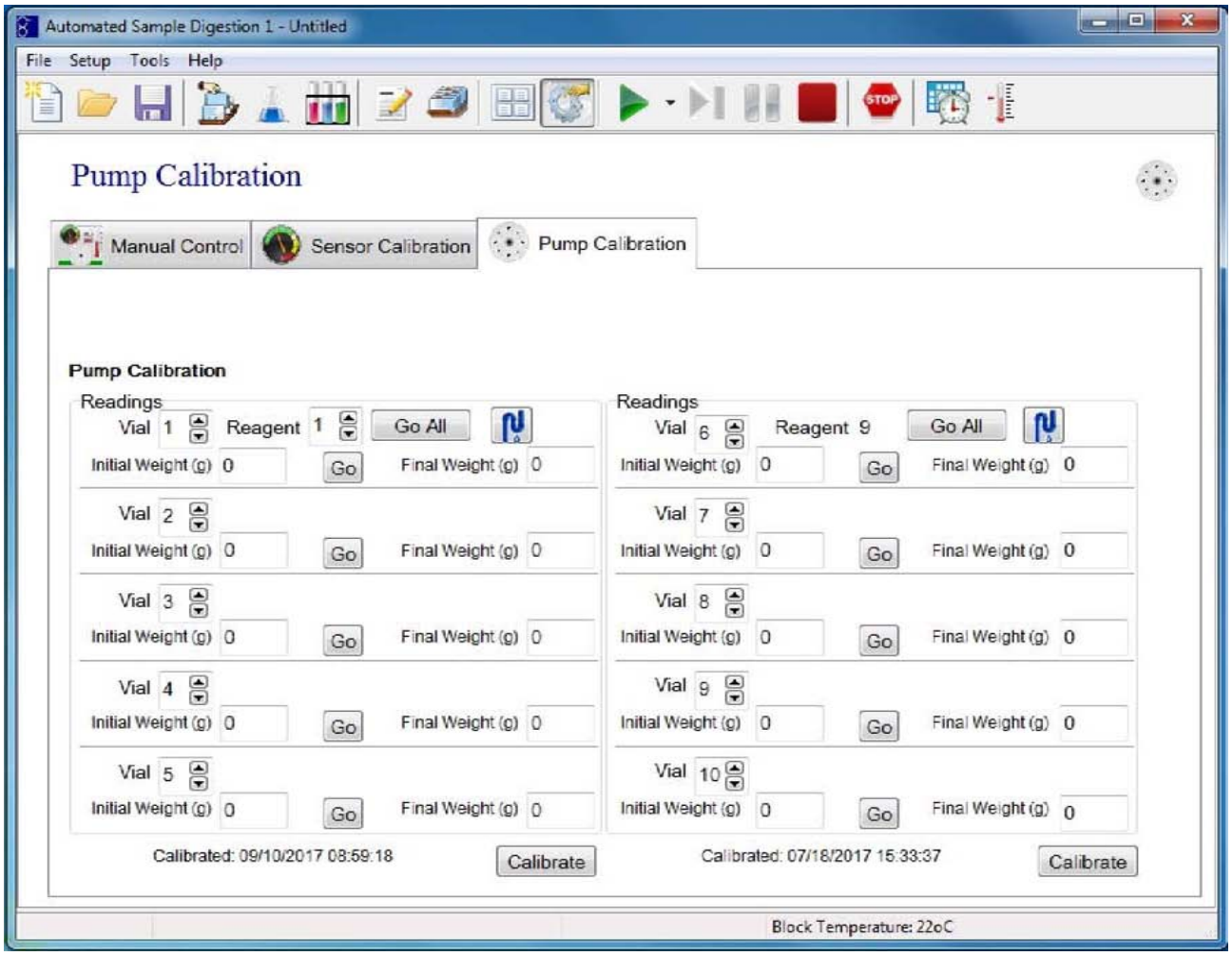


Figure 5: Digestion Method Window for DEENA (Example)

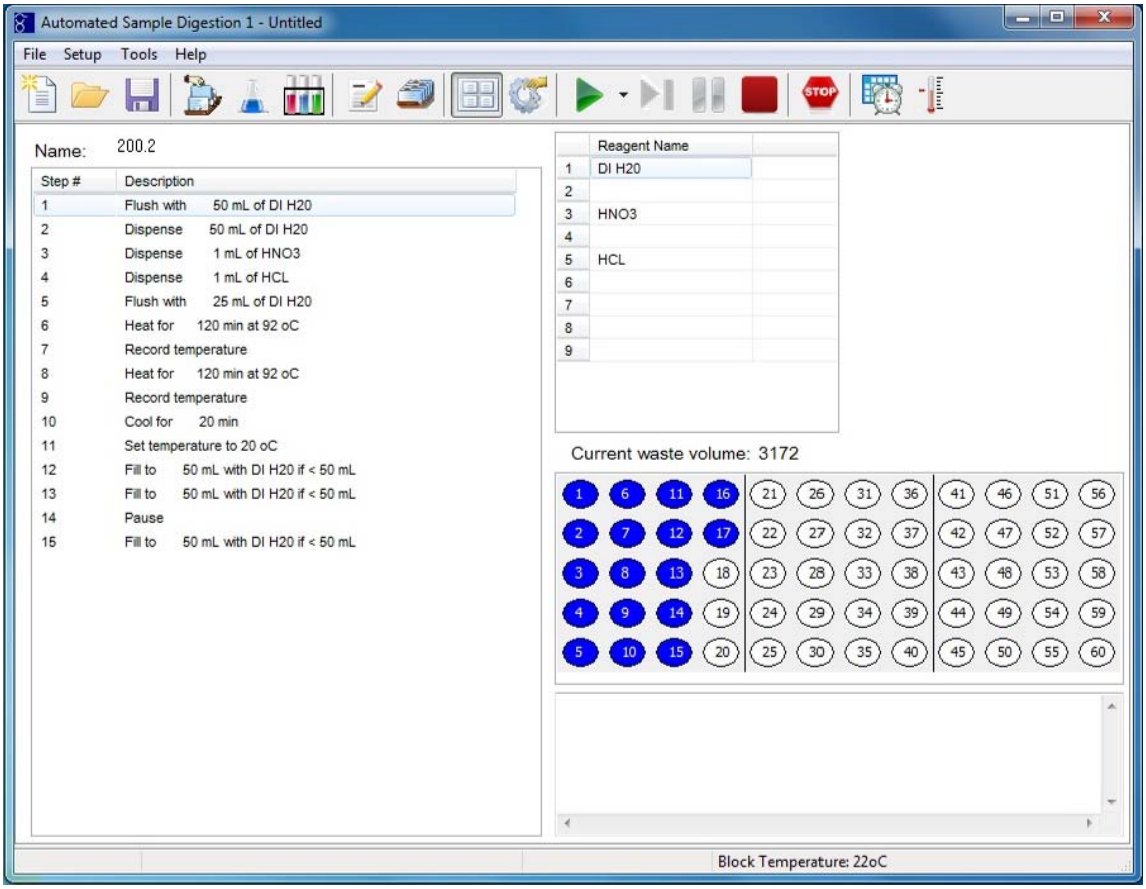
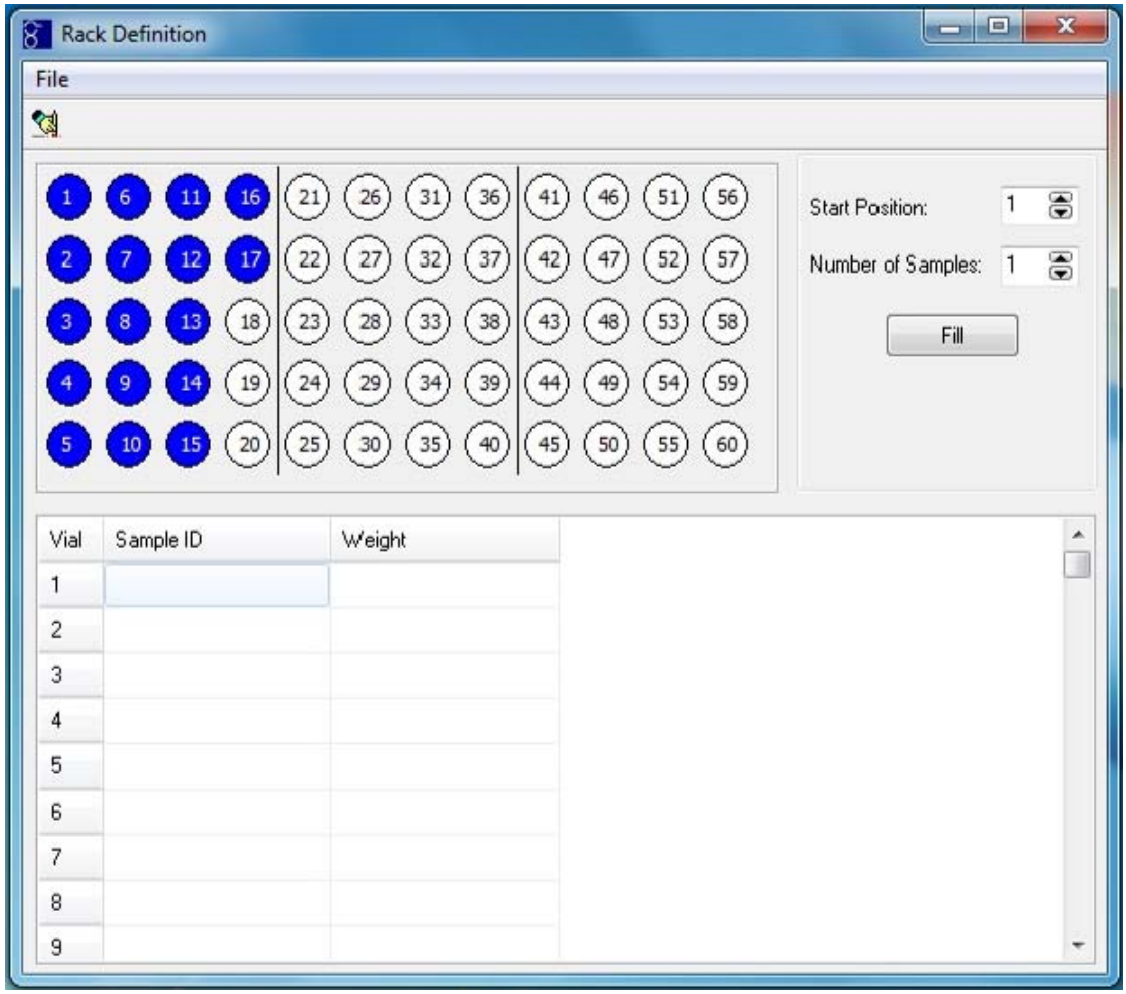


Figure 6: Digestion Rack Window for DEENA



Revision Number	Description of Changes	Date
05	Document changed to incorporated administrative requirements of ISO 17025 and QSM 5.0. Descriptions of changes have not been tracked in previous versions of this document.	03/12/2015
5.1	Modified tissue statement in section 11.2	03/31/2016
6.0	Included DEENA Automated Digester Procedure	09/15/2017
6.1	Updated to include use of Teflon beads for MBS, include lab shall acid pretreat syringe filters	05/25/18
6.2	Administrative changes and reference updates.	05/29/2019

STANDARD OPERATING PROCEDURE

MT 009 Inductively Coupled Plasma (ICP) Emission – ICP-OES 6000

Review Date: 04/15/19

04/16/2019

Technical Review by: Date

04/16/2019

Approved by: Quality Assurance Date

1.0 Identification of Test Method

1.1 This procedure is used for the analysis of trace elements (metals) following EPA SW 846 Methods 6010B and/or 6010C/ and or 6010D (Inductively Coupled Plasma –Atomic Emission Spectrometry) and Method 200.7.

2.0 Applicable Matrix or Matrixes

2.1 This method is applicable to the determination of various metals in drinking water, surface water, groundwater, sludge, soils, and industrial wastes.

3.0 Detection Limits

3.1 Method detection limits (MDLs) are determined annually and results vary from element to element. Procedures for conducting MDL studies can be found in SOP QA023.

4.0 Scope and Application

4.1 Metals in solution can be readily analyzed by atomic emission using an Inductively Coupled Plasma (ICP) spectrometer. All matrices, excluding filtered groundwater samples and drinking waters with a turbidity less than 1 NTU, will require a digestion prior to analysis.

5.0 Method Summary

5.1 If necessary, prior to analysis, samples are digested using an approved method. See SOPs MT003 and MT007for further information on sample digestion.

5.2 This method describes multi-element determinations using an ThermoScientific iCAP 6000 Series ICP-OES which use an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Most Samples are liquids that are pumped through a nebulizer to produce a fine spray. The large droplets are removed by a spray chamber and the small droplets then pass through to the plasma. The solvent is evaporated. The residual sample is decomposed to atoms and ions that become excited and emit characteristic light which is measured, giving measurement of the concentration of each element type in the original sample. Control of the spectrometer is provided by the PC based iTeva software (refer to the Thermo ICP-OES software manual). Samples are routinely analyzed using an internal standard solution of 50 mg/L Yttrium to eliminate certain matrix interference problems. Line switching is also used to extend the dynamic range of an element.

5.3 The data is exported to the LIMS system and reviewed by the analyst.

Following analyst review, the data is given to a qualified reviewer for complete data review. After the data has been reviewed and it is determined that it is valid data, the reviewer sends the data to the "validated" mode in the LIMS system.

6.0 Definitions

6.1 For full definitions on all terms applicable to this method, see the Quality Assurance Manual (QAM).

6.2 For a list of common acronyms and abbreviations, see QAM.

6.3 Low-Level Calibration Check Standard (LLCCV) For DOD-QSM samples a low level standard shall be analyzed daily at or below the LOQ for the element(s) being analyzed. The acceptance criterion is +/- 20% of the expected value.

6.4 ICS-A 1, 2, 3, 4 (Interelement Correction Standard A - 1, 2, 3, 4): A standard containing the elements Al, Ca, Fe, and Mg at 500 mg/L, and Ce and V at 10 mg/L. ICSA-1 contains Mn at 10 mg/L. ICSA-2 contains Ba, Be, and Sn at 10mg/L. ICSA-3 contains Cr, Co, Cu, and Sn at 10 mg/L. ICSA-4 contains Ni and Ti at 10 mg/L. These standards are analyzed following the ICAL at the beginning of the run to determine if interelement correction factors are correctly compensating for interference from these elements on other analyte lines.

6.5 Linear Dynamic Range (LDR) – The upper limit of the linear dynamic range is established for each wavelength utilized by determining the signal responses from a minimum of three different concentration standards across the range. One of these will be near the upper limit of the range. The ranges used for the analysis of samples are judged by the analyst from the resulting data. The data and calculations are kept on file. The upper range limit is an observed signal no more than 10% below the level extrapolated from the lower standards. Determined analyte concentrations above the upper range limit are diluted and reanalyzed. New dynamic ranges are determined whenever there is a significant change in instrument response. For analytes that routinely approach the upper limit of the range, the range will be checked biannually. For analytes that are known interferents and exceed the dynamic range, the analyst will check that IEC's have been correctly applied. DOD-QSM requires that a LDR (or high level check standard) study be perform at least every six months.

6.6 ICS-A (Interelement Correction Standard-A): A standard containing the elements Al, Ca, Fe, and Mg at 500mg/L and Ce at 10 mg/L,. This standard may also contain other program specified elements (i.e. copper and nickel are included at 10 mg/L for the drinking water analysis of 200.7) This standard is analyzed when using method 200.7 following the ICV at the beginning of the run to determine that interelement correction factors are correctly compensating for interference from these elements on other analyte lines.

6.7 ICS-AB (Interelement Correction Standard-AB): A standard containing the elements Al, Ca, Mg, and Fe at 500mg/L and all other elements at 500ug/L.

This standard is analyzed following the ICV at the beginning of each run. It is analyzed to determine that the IEC are correctly preventing interference by these elements on the measurement of other analytes. PDS (Post Digestion Spike): When a serial dilution or matrix spike falls outside of the acceptance limits a post digestion spike is used to determine if the sample digestion matrix is interfering with the analysis of the analyte. The sample is spiked at a level similar to that of the matrix spike.

6.8 SD (Serial Dilution Analysis): A sample is diluted 5x with method blank solution and analyzed. The diluted result and the undiluted result should agree within a limit of precision defined by the program or client QAPP.

6.9 IDL (Instrument Detection Limit); A series of blanks analyzed during initial setup or after significant changes, or as per DOD-QSM requirements. The limits established shall be < LOD for any given element.

7.0 Interferences

7.1 Background emission and stray light are corrected using background correction. See ICP 6000 Series operator's manual for further instructions on background correction application.

7.2 Spectral overlaps are corrected for using interelement correction factors (IEC). When IEC are used, the interfering elements must be analyzed along with the elements of interest. The accuracy of IEC shall be verified daily by analyzing the ICSAB. All IEC factors shall be updated every six months or when an instrumentation change occurs; such as, changing a torch, nebulizer, injector, or plasma conditions.

7.3 Physical interferences such as viscosity are minimized by using an internal standard. Post digestion spike and serial dilutions help to determine if physical interferences are present.

7.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Chemical interferences are not normally seen during ICP analysis and are highly matrix dependent.

7.5 Memory interferences occur when a sample of high analyte concentration does not thoroughly rinse prior to the analysis of the next sample. This causes elevated readings for that analyte in the subsequent sample. Memory effects can be minimized by rinsing at least 60 seconds between samples.

7.6 Switching to an alternate wavelength is also an option to solve an interferent.

8.0 Safety

8.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

8.2 Insure that waste collection vessels contain enough room to accommodate all wastes that will be produced during the operation of the instrument.

9.0 Equipment and Supplies

9.1 ICP 6500, Cetac autosampler, computer, & network printer.

9.2 Argon (Airgas-liquid high purity or gaseous pre-purified grade or equivalent).
9.3 Class A volumetric flasks and pipettes (Chemglass or equivalent).
9.4 Disposable 15-mL polystyrene culture tubes.
9.5 100 ul pipette (Eppendorf or equivalent).
9.6 10-mL pipette (Eppendorf or equivalent).

10.0 Reagents and Materials

10.1 Reagent Single element stock metals standards (Vendors =CPI/Ultra Scientific or equivalent) at either 10,000 or 1000 ug/mL Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb Sb Se Tl, V ,Zn, Y, Na, Si, Ti, Sr, Sn, B, Li, K, P, S, Hg, Ce, and La.
10.2 Nitric acid, conc. (Fisher, Trace Metals grade or equivalent)
10.3 Hydrochloric acid, (Fisher, Trace Metals grade or equivalent)
10.4 Deionized water (Milli Q, > 10 mega ohm).
10.5 Interference A (SPEX Certiprep, Cat.# INT-A1 or equivalent) =5000 ug/mL Al, Ca, Mg , 2000ug/mL Fe
10.6 Custom Assurance Std 23 (SPEX Certiprep, Cat.# XCTWI-5-500 or equivalent) = 100 ug/mL Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti Tl V, and Zn.
10.7 Custom Assurance Std 3(SPEX Certiprep, Cat.# XCTWI-4-500 or equivalent) = 100 ug/mL Ag, Be, and Cd
10.8 Custom Assurance Std_(SPEX Certiprep, Cat.# XCTWI-1-500 or equivalent) = 20000 ug/mL Ca, 10000ug/mL Mg, Na.
10.9 Custom Assurance Std Spike (SPEX Certiprep, Cat.# XSPIKE-1-250 or
10.10 equivalent)=200 ug/mL Al, As, Ba, Se and Tl,
100 ug/mL Fe
50 ug/mL Co, Mn, Ni, Pb, Sb ,V, Zn.
25 ug/mL Cu
20 ug/mL Cr
5 ug/mL Ag, Be, Cd

See Section 13 and Appendix A, B, C and D for instructions on making the working standards.

11.0 Sample Preservation and Storage

11.1 Samples must be preserved and analyzed within holding times stated in chart. Liquid samples are stored on shelves in the Laboratory warehouse and soil samples are stored in a walk-in refrigerator unit.

	Liquids	Solids	
Preservative:		pH <2 with HNO_3	4^oC (+/-2)
Hold Time:		180 days	180 days

12.0 Quality Control

12.1 This SOP is designed to follow a variety of different projects and programs

requirements. Table 3 is designed to illustrate the control steps and provisions required to adequately producing acceptable data.

12.2 Contract Specific Sample Analysis: For certain samples, limits are specified by the QAPP (Quality Assurance Project Plan) associated with a given project. For these samples follow the limits specified in the QAPP for that project.

12.3 New or unusual matrices: It is recommended that whenever a new or unusual sample matrix is encountered, a serial dilution and post digestion (bench) spike be performed prior to reporting results. These tests will ensure that neither positive nor negative interferences are affecting sample results.

12.3.1 Serial Dilution: If the analyte concentration is sufficiently high (minimally a factor of ten above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within +/- 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

12.3.2 Post digestion/bench spike addition (Table 2): An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within +/- 25% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike recovery falls outside these limits, a matrix effect should be suspected.

12.4 ICS-A 1, 2, 3, 4 (Interference check solution: interference only) ICSA - 500 mg/L for Al, Ca, Mg, and Fe, and 10 mg/L for Ce and V. ICSA-1 Mn at 10 mg/L, ICSA-2 Ba, Be, and Sn at 10 mg/L, ICSA-3 Cr, Co, Cu, and Mo at 10 mg/L, ICSA-4 Ni and Ti at 10 mg/L. These samples must be analyzed at the beginning of the analytical run before the ICSAB. Recovery acceptance criteria for interfering analytes are +/- 20% true value. All other analytes need to be <LOQ. If the recovery/result is outside the acceptable range, corrective action must be taken before samples can be analyzed. Check placement of background correction points and IECs as a place to start trouble shooting.

13.0 Calibration and Standardization

13.1 The default calibration for TAL (Target Analyte List) plus list (excluding Na and K) of metals for DOD-QSM and routine work is a multi-point calibration method called ‘DOD calibration’ which uses 12 mixed standards and a calibration blank.

13.2 The default calibration for the metals Sodium and Potassium for, DOD-QSM and routine work is a multi-point calibration method called ‘Sodium and Potassium’ which uses 8 mixed standards and a calibration blank.

13.3 The default calibration for the metal Boron for DOD-QSM and routine work is a multi-point calibration method called ‘Boron’ which uses 5 standards and a calibration blank

13.4 The default calibration for the metal Lithium for DOD-QSM and routine work is a multi-point calibration method called ‘Lithium’ which uses 7 standards

and a calibration blank. Refer to section 11.0 for further instructions on how to perform the calibration.

Note: See Appendix A for preparations of calibration standards and blank for the DOD calibration method calibration. See Appendix B for the preparation of the calibration standards and blank for the Sodium and Potassium method calibration. See Appendix C for the preparation of the calibration standards and blank for the Boron calibrations. See Appendix D for the preparation of the calibration standards and blank for the Lithium calibration. See Tables 4 (a, b, & c), 5, 6, and 7 for individual element calibration concentrations/ranges.

13.5 Calibration Blank: Into a 1 L. volumetric flask, add 750 mL of Milli-Q water and 10mL of conc. HNO3 and 10mL HCl. Mix, dilute to volume with Milli-Q H2O. Transfer to a clean 1 L. Nalgene bottle. Prepare every 6 months or as needed.

13.6 Yttrium Internal std (Used for all methods) : Into a 2000mL volumetric flask, add 500mL of Milli-Q H2O, 10 ml 10,000 mg/L Yttrium standard dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 2L Nalgene bottle. Prepare every 6 months or as needed. Concentration = 50 mg/L Yttrium solution.

13.7 Initial/Continuing Calibration Verification (ICV/CCV): Into a 1000mL volumetric flask, add 500mL of Milli-Q water, 10 mL of conc. HNO3 and 10mL HCl. Add the following:

10 mL Custom Assurance standard Spike or Equivalent
0.5mL Mo 1000mg/L
2 ml Interferents-A-SPEX Certiprep or equivalent
1 ml Ce 1000 std

Dilute to volume with Milli-Q water, mix and transfer to a clean 1 L Nalgene bottle. Make new every 6 months or as needed.

Concentration	Analyte
50ug/L	Cd, Be
100ug/L	Ag
200ug/L	Cr
250ug/L	Cu
500ug/L	Co, Mn, Mo, Ni, Pb, Sb, V, Zn
2000ug/L	Ba, As, Tl, Se
5,000ug/L	Fe
10,000ug/L	Ca, Mg
12,000ug/L	Al

13.8 Interference Check Solution (ICSA): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H_2O, 5 mL of conc. HNO_3 and 5mL conc. HCl. Add the following stock solutions in the volumes listed:

50 mL Spex Certiprep Interferents A or equivalent

15 ml Fe 10,000 mg/L or equivalent
5 mL V 1000 mg/L or equivalent
5 mL Ce 1000 mg/L or equivalent

Dilute to volume with Milli-Q H_2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration	Analyte
500,000 ug/L	Al, Ca, Mg, Fe
10,000 ug/L	V
10,000 ug/L	Ce

Interference Check Solution (ICSA 1): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H_2O, 5 mL of conc. HNO_3, and 5mL conc. HCl. Add the following stock solutions in the volumes listed:

5 mL Mn 1000 mg/L or equivalent

Dilute to volume with Milli-Q H_2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration	Analyte
10,000 ug/L	Mn

Interference Check Solution (ICSA 2): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H_2O, 5 mL of conc. HNO_3, and 5mL conc. HCl. Add the following stock solutions in the volumes listed:

5 mL Ba 1000 mg/L or equivalent
5 mL Be 1000 mg/L or equivalent
5 mL Sn 1000 mg/L or equivalent

Dilute to volume with Milli-Q H_2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration	Analyte
10,000 ug/L	Ba
10,000 ug/L	Be
10,000 ug/L	Sn

Interference Check Solution (ICSA 3): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H_2O, 5 mL of conc. HNO_3, and 5mL conc. HCl. Add the following stock solutions in the volumes listed:

5 mL Cr 1000 mg/L or equivalent
5 mL Cu 1000 mg/L or equivalent
5 mL Co 1000 mg/l or equivalent
5 mL Mo 1000 mg/L or equivalent

Dilute to volume with Milli-Q H_2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration	Analyte
10,000 ug/L	Cr
10,000 ug/L	Cu
10,000 ug/L	Co
10,000 ug/L	Mo

Interference Check Solution (ICSA 4): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H_2O, 5 mL of conc. HNO_3, and 5mL conc. HCl. Add the following stock solutions in the volumes listed:

5 mL Ni 1000 mg/L or equivalent
5 mL Ti 1000 mg/L or equivalent

Dilute to volume with Milli-Q H_2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration	Analyte
10,000 ug/L	Ni
10,000 ug/L	Ti

13.9 Interference Check Solution (ICSAB): Into a 500 mL volumetric flask, add 300 mL of Milli-Q H2O, 5 mL of conc. HNO3 and 5 mL conc. HCl. Add the following stock solutions in the volumes listed:

50 mL Spex Certiprep Interferent A or equivalent
15 ml Spex Certiprep Fe 10,000 mg/L or equivalent
2.5 ml Custom Assurance std 23 or equivalent
2.5 ml custom assurance std 3 or equivalent

Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean 500 mL Nalgene bottle. Prepare every 6 months or as needed.

Concentration	Analyte
500,000 ug/L	Al, Ca, Mg, Fe
500 ug/L	Ag, As, Ba, Be Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sb, Tl, V, Zn

13.10 CRDL/MRL/LLOQ solution: Concentrations needed depend on the CRDL/MRL/LLOQ of a given contract.

14.0 Procedure

14.1 Instrument start-up procedure:

14.1.1 Open valve at argon tank, turn on chiller and instrument. For best results, the instrument should be on and with an argon purge for at least 24 hours

14.1.2 Inspect pump tubing on instrument and on autosampler and change if necessary.

14.1.3 Fill DI rinse reservoir with DI water and preserve with HNO3 to1%.

14.1.4 Open up the ITeva software on the PC. Choose user, wait until instrument initializes.

14.1.5 Plasma startup and shutdown: Refer to the ICAP 6000 Series ICP-OES Spectrometer Operator manuals pages 11-1 thru 11-4. After plasma startup check the “Debug Wavelength Check” at the bottom of the ITeva control center. The absolute value of x and y #s should be less than 5, if not, stop and call Thermo service.

14.1.6 After a 30-minute warm-up period, check condition of nebulizer. Put pump tube into a 100mg/L solution Yttrium Std. With the lights off and after enough time has elapsed for the Yttrium standard to reach the plasma, a red cone should be noticeable in the center of the plasma. If the nebulizer is in good condition and the nebulizer gas flows are set properly, the red cone should project about 2mm beyond the coils. If not, check the settings, the pump tubes, and inspect the nebulizer under a microscope for any obstructions or breakage.

14.2 To create an autosampler sequence:

14.2.1 Refer to the ICAP 6000 Series ICP-OES Spectrometer Operator manuals pages 11-9 thru 11-11 to start an autosampler sequence.

14.2.2 Add all samples, LCS, Blanks, MS-MSD, etc. in order of program, agency or client request.

14.2.3 Print Autosampler Table: This will be used when preparing all samples and standards.

14.2.4 Using the printed autosampler table sheet, prepare all standards, QC samples, and samples in their designated positions in the autosampler. Prepare any bench spikes and place them in autosampler. Calibration standards, CCV, ICV, CCB, ICB and ICSAB all go into 50 ml vials in the designated S-# positions of the autosampler. All others are poured into 15 ml plastic vials into the designated areas within the 60 position racks.

14.3 Calibration and Analysis.

14.3.1 Once all calibration standards have been placed in the autosampler make sure the autosampler is initialized by clicking on the autosampler icon and the sequence is saved and then press the yellow arrow icon to start the calibration and prepare the remaining samples as the calibration is being carried out.

14.4 Instrument shutdown

14.4.1 If run will not be finished during work hours, program the instrument to shut down at the end of the analytical run. When setting up on the sequence page click the "End Action (after all sequences) Box to "Shutdown Plasma". This will shut down the plasma.

14.4.2 For manual shutdown go to the flame icon in the bottom right corner and click, and then select the plasma off icon. After the plasma is shutdown loosen the pump tubes and shut off the chiller.

15.0 Calculations

15.1 Sample Calculations:

Liquid Concentration (ug/L) = A x C

$$\text{Solid Concentrations (mg/kg)} = \frac{A \times B \times C}{D \times E}$$

Where: A = instrument reading for sample (ug/L)
B = total volume of digestion (L)
C= dilution factor, if necessary (ex. For a 1 to 10 dilution, C = 10)
D = amount of sample used in digestion (g)
E = percent solids/100, if necessary (fraction equivalent)

15.2 Spike Recovery Calculations:

$$\text{LCS Recovery (\%)} = \frac{(\text{Result obtained}) \times 100}{(\text{Spike amount})}$$

$$\text{MS/MSD Spike Recovery (\%)} = \frac{(\text{Spiked sample conc.} - \text{Sample conc.}) \times 100}{(\text{Spike amount})}$$

$$\%\text{RPD} = \frac{(MS - MSD) \times 100}{(MS + MSD)/2}$$

Where: MS = Matrix spike concentration obtained
MSD = Matrix spike duplicate concentration obtained

15.3 "Total Hardness" (by calculation) can be determined by using the values for calcium and magnesium obtained by this procedure. The "Total Hardness" value is calculated in the LIMS system using the following equation:

Total Hardness (mg/L) or Hardness equivalent $CaCo^3/L$ =

2.497[Ca mg/L} + 4.118[Mg mg/L]

15.4 Ferric/Ferrous Iron (by calculation can be determined by using the values for Total Iron (Fe) and Dissolved Iron obtained by this procedure. The "Iron III" or Ferric Fe value is calculated in the LIMS system using the following equation:

Total Fe – Dissolved Fe = Ferric Fe (Iron III)

16.0 Method Performance

16.1 Certified standard solutions, properly used instrumentation, and analyst experience and expertise are critical elements in producing accurate results. Standards and instrument performance are continually checked by analyzing external performance test samples provided by the appropriately accredited agencies. Internal blind spikes are also utilized to check analyst performance.

16.2 Initial demonstration of capability (IDC) is another technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of 4-5 laboratory control spikes for each matrix and sample type. After analysis, the analyst calculates the average recovery (AR) and the relative standard deviation (RSD) of the recoveries for each analyte. In the absence of specific criteria found in the EPA methods or project specific limits, the default criteria of 70-130% recovery and 20 % RSD are used until internal limits are generated. (See SOP QA-022 for specifics)

16.3 Proper instrument maintenance is another means to ensure adequate method performance.

16.3.1 Pump tubing and rollers: Ensure that the pump rollers turn freely. Inspect pump tubing daily and replace when it starts failing to retain its shape.

16.3.2 Drain line: Spray chamber drain line must flow unimpeded directly into waste jug. Make sure line is draining properly.

16.3.3 Spray Chamber: If the spray chamber becomes dirty, the sample waste may not drain properly. Remove and wash with hot soapy water, then rinse with DI H_2O.

16.3.4 Torch and O-rings: The O-rings surrounding the torch may need to be replaced if the plasma becomes unstable or internal standard emission counts fall off. See ICP6000 manual for technique. Torch needs to be cleaned occasionally with aqua regia followed by sonication. See sections 5 and 6 in the "ICAP 6000 Series ICP-OES Spectrometer Operating Manuals" for further assistance if needed.

17.0 Pollution Prevention

17.1 See QAM.

18.0 Data Assessment and Acceptance Criteria for QC Measures

18.1 When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. The analyst will review the data to ensure QC is acceptable and that exceedances are addressed. Acceptable data is then captured into the LIMS system (See SOP MT-010 Data Capture for instructions on data capture).

18.2 All manual integrations will be reviewed for validity (See SOP QA-016 Manual Integrations for specifics).

18.3 After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist (FMT9-01) for data review guidance.

18.4 Once analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

18.5 After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

18.6 A paper copy of the data is then filed or archived. The package includes the checklist, the sequence run log, and a copy of the bench sheet (if applicable), the LIMS run log, and verification of calibration data.

19.0 Corrective Measures for Out-of-Control Data

19.1 See QAM.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 See QAM

21.0 Waste Management

21.1 Samples are routinely held for up to six weeks from analysis date before they enter the waste stream. Waste disposal of samples and standards follows the procedures documented in the Laboratory Waste Disposal SOP (WS-001).

22.0 REFERENCES

22.1 Test Methods for Evaluating Solid Waste, EPA, SW-846, Method 6010B, rev. 2, December 1996.

22.2 Test Methods for Evaluating Solid Waste, EPA, SW-846, Method 6010B, rev. 3, February, 2000.

22.3 Test Methods for Evaluating Solid Waste, EPA, SW-846, Method 6010C, rev. 3, February, 2007.

22.4 Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, Method 200.7, rev. 4.4, 1991.

22.5 USEPA - Contract Laboratory Program, Statement of Work for Inorganic Analysis, ILM04.0.

22.6 ICAP 6000 Series ICP-OES Spectrometer Operator's Manual, Thermo Electron (registration number 441506).

22.7 Thermo Electron Corporation Training Manual iCAP 6000 Series.
22.8 Standard Methods For the Examination of Water and Wastewater, 21st Edition, 2340B-Hardness by Calculation, 2005.
22.9 CT Laboratories Quality Manual, current revision.
22.10 Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.0, July 2013 or most recent revision.
22.11 Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.1, Sept 2017 or most recent revision.
22.12 National Environmental Laboratory Accreditation Conference (NELAC), 2003 NELAC Standard Chapters 1 to 6, EPA/600/R-04/003, June 5, 2003 or most recent version.
22.13 ISO. 2005. General requirements for the competence of testing and calibration laboratories. ISO17025.
22.14 Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.
22.15 Test Methods for Evaluating Solid Waste, EPA, SW-846, Method 6010D, rev 4, July, 2014.

23.0 Appendices

Table1: Spike, LCS, & LFB Analysis- ICP
Pre-digestion Spikes

Element	Spike Amt. mL of	Spike Stock A, B, C	Stock Conc. mg/L	Final Vol. mL	Expected Conc. ug/L
Aluminum	1	**A**	200	50	4000
Antimony	1	**A**	50	50	1000
Arsenic	1	**A**	200	50	4000
Barium	1	**A**	200	50	4000
Beryllium	1	**A**	5	50	100
Cadmium	1	**A**	5	50	100
Calcium	0.5	**C**	20,000	50	200000
Chromium	1	**A**	20	50	400
Cobalt	1	**A**	50	50	1000
Copper	1	**A**	25	50	500
Iron	1	**A**	100	50	2000
Lead	1	**A**	50	50	1000
Manganese	1	**A**	50	50	1000
Magnesium	0.5	**C**	10,000	50	100000
Molybdenum*	0.1	**B**	1000	50	2000
Nickel	1	**A**	50	50	1000
Selenium	1	**A**	200	50	4000
Silver	1	**A**	5	50	100
Thallium	1	**A**	200	50	4000
Vanadium	1	**A**	50	50	1000
Zinc	1	**A**	50	50	1000

Spike Solutions ***		
Supplier	**Lot #/ std**	**Stock**
SPEX Certiprep or equiv.	SPIKE 1-500	**A**
Molybdenum * or equiv.	1000 mg/L	**B**
Custom Std***	SPEX	**C**

- * Addition of Boron, Lithium, Silicon, Tin, Strontium, Titanium, and Tungsten at 0.1 ml each of a 1000 mg/L solution from SPEX Certiprep or equivalent.
- ** Addition of Potassium at 0.5 ml of a 10,000 mg/L solution from SPEX Certiprep or equivalent.
- *** Sodium is also included in this standard at 10,000 mg/L

Table 2: Bench Spike Analysis-ICP
Post Digestion/ Bench Spikes

Element	Spike Amt. ML of	Spike Soln.	Stock Conc. mg/L	Final Vol. mL	Expected Conc. ug/L
Aluminum	0.2	**A**	200	10	4000
Antimony	0.2	**A**	50	10	1000
Arsenic	0.2	**A**	200	10	4000
Barium	0.2	**A**	200	10	4000
Beryllium	0.2	**A**	5	10	100
Cadmium	0.2	**A**	5	10	100
Calcium	0.2	**B**	20,000	10	400000
Chromium	0.2	**A**	20	10	400
Cobalt	0.2	**A**	50	10	1000
Copper	0.2	**A**	25	10	500
Iron	0.2	**A**	100	10	2000
Lead	0.2	**A**	50	10	1000
Manganese	0.2	**A**	50	10	1000
Magnesium	0.2	**B**	10,000	10	200000
Molybdenum	0.02	**C***	1000	10	2000
Nickel	0.2	**A**	50	10	1000
Selenium	0.2	**A**	200	10	4000
Silver	0.2	**A**	5	10	10
Thallium	0.2	**A**	200	10	4000
Vanadium	0.2	**A**	50	10	1000
Zinc	0.2	**A**	50	10	1000

Standard Source * **	
Supplier	
SPEX	**A**
SPEX Custom Std	**B**
Molybdenum-1,000 mg/L Std*	**C***

- * Addition of Boron, Lithium, Silicon, Tin, Strontium, Titanium, and Tungsten at 0.02 ml each of a 1000 mg/L solution from SPEX Certiprep or equivalent.
- ** Addition of Potassium and Sodium at 0.1 ml of a 10,000 mg/L solution from SPEX Certiprep or equivalent.

Table 3: Summary of Quality Control Requirements

QC Type	Frequency	Conc. Level	1. *Acceptance Criteria*	2. *Corrective Action*
Linear Dynamic Range(LDR) or high level check standard	At initial set up and checked every 6 months with a high standard at the upper limit of the range	High point of calibration curve	Recovery (Rec.) within ± 10% of true value.	Data cannot be reported above the high calibration range without an a established/passing high level check standard
Initial Calibration (ICAL) for all analytes	Daily ICAL prior to sample analyst	Table. 4a.	If more than one calibration standard used, r2 ≥ 0.99.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	1 per calibration	Mid. Calib. Range	EPA 200.7 Rec.: 95-105% SW846:90-110% Or Project/Program Specific	Terminate run. Correct the problem before proceeding
Initial Calibration Blank (ICB)	Immediately after the ICV	<MDL	SW846: < 3x IDL EPA 200.7: < MDL DOD-QSM < MDL or Project / Program Specific	Terminate analysis and correct the problem before proceeding.
Method Blank (MB)	1 per batch of 20 samples	<MDL	200.7: < MDL SW846: < 2x MDL DOD-QSM: <1/2 MRL or Project / Program Specific	Access data and reanalyze/re-prepare the MB and affected data or flag “B” analyte detected in Method Blank when insufficient sample remains
Laboratory Control Sample (LCS)	1 per batch of 20 samples	Mid. Calib. Range	In-house limits or, default Rec.: 80-120% EPA200.7 ; 85-115% or Project / Program Specific	Terminate analysis: correct problem before proceeding.
Continuing Calibration Verification (CCV)	1 after every 10th sample	Mid. Calib. Range	SW846: Rec.: 90-110% EPA 200.7: 90-110% CLP:90-110%	Rerun once if fail Recalibrate and reanalyze all samples back to the last acceptable CCV or ICV

Low Level Continuing Calibration Verification (LLCCV)	Daily	LLCCV should be less than or equal to the LOQ.	All reported analytes within ± 20% rec. of the true value.	No samples shall be analyzed without a valid Low-Level Calibration Check Standard (LLCCV). If the concentration of the lowest calibration standard is less than or equal to the LOQ, the lowest standard may be re-quantified against the calibration curve as a LLCCV. Otherwise, a separate standard must be analyzed as the LLCCV prior to the analysis of any samples.
Continuing Calibration Blank (CCB)	Immediately following each CCV	<MDL	SW846: < 3x IDL EPA 200.7: < MDL DOD-QSM < MDL or Project / Program Specific	Reanalyze all samples back to the last acceptable CCB or flag "B" analytes detected
Interference Check Solution ICSA-1,2,3,4	Immediately after the ICAL	500 mg/L Al, Ca, Fe, Mg. 10 mg/L Ce, V, Mn Ba, Be, Sn, Cr, Co, Cu, Mo, Ni, Ti. or program specific	Recovery: 80-120% for Interference Elements. ABS of analytes not included must be < LOQ or Project / Program Specific	Terminate analysis, correct problem & reanalyze all samples back to last good ICSA/ICSAB
Interference Check Solution A (ICSA)	Immediately After LCS (& before final CCV if required by program / project specific QAPP)	500mg/L Al, CA,FE, Mg, or program specific	Rec.: 80-120% for Interference Elements ABS of analytes not included must be < 2X MRL or Project / Program Specific	Terminate analysis, correct problem & reanalyze all samples back to last good ICSA/ICSAB

Interference Check Solution AB (ICSAB)	Immediately After ICSA (& before final CCV if required by program / project specific QAPP)	500mg/L Al, CA, FE,MG Other elements 500ug/L	Rec.: 80-120% for All Elements	Terminate analysis, correct problem & reanalyze all samples back to last good ICSA/ICSAB
MS	One per batch (20 samples) per matrix EPA 200.7-one per 10 samples	See Table 1 spike chart	1. In-house limits: default 70-130 % Rec. 2. DOD-QSM: Use specified LCS limits. 3. LCG: 75-125 % Rec. when [matrix] is <4x[spike] 4. EPA 200.7 default 70-130% Rec. or in-house generated limits.	1. Reanalyze an alternative sample or perform a PDS, if MS and PDS fail qualify data as to matrix effect. 2. DOD-QSM: Used for matrix evaluation only. Determine source of difference (i.e. serial dilution/PDS). Reanalyze or qualify data as per client/ project requirement. 3. LCG: If MS fails and sample results are < 5x the MRL run a PDS. If sample results are > 5x the MRL perform a serial dilution.
MSD or Matrix Dup. (MD)	1. In-house & QSM-DOD: one MSD or MD per batch or matrix. 2. EPA 200.7-one per 10 samples	See Table 1 spike chart	1. In-house limits: default 70-130 % Rec. RPD = 20% 2. DOD-QSM: Use specified LCS limits for MSD. RPD = 20 % for MS/MSD or MD.	1. Perform PDS, if MSD and PDS fail qualify data as to matrix effect. 2. DOD-QSM: Used for matrix evaluation only. Determine source of difference (i.e. serial dilution/PDS). Reanalyze or qualify data as per client/ project requirement.

Serial Dilution Analysis (SD)	1. In-house: Analyzed on the sample with a PDS failure. 2. DOD-QSM: Analyzed with each batch of samples. .	5 fold dilution of chosen sample	RPD within 10% of value of diluted and undiluted sample, but only if sample conc. 1. In-house: > 10x LOQ 2. DOD-QSM: > 50x the MDL	1. In-house: Qualify data only if sample result is > 10x the LOQ. 2. Analyze a PDS if sample result is > 50x the MDL.
Post Digestion Spike (PDS)	1. In-house: Upon failure of MS or MSD. 2. DOD-QSM: When the SD test fails or all sample results < 50x the MDL and there is an MS or MSD failure.	Between 10 and 100 times the MDL	1. In-house: 80-120% Rec. 2. DOD-QSM : 80-120% Rec.	1. In-house: Qualify for matrix interference or if requested analyze by MSA. 2. DOD-QSM: Run samples by MSA or ISA or qualify data using program/project specified criteria.
Method of Standard Additions (MSA) or Internal Standard Calibration (ISA)	1. In-house: When requested. 2. DOD-QSM: After the failure of a PDS.	Minimum of 3 standard levels and the unspiked sample	N/A	Document the use of an MSA or ISA

Table 4a. TAL list Concentrations/Ranges for ICP ug/L

Element, Wavelength and Order	Calibration Standards																											
	Blank		CalStd1=0.25		CalStd2=0.5		CalStd3=1		CalStd4=5		CalStd5=10		CalStd6=20		CalStd7=50		CalStd8=100		Ca									
	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?									
Ag 328.068 {103}	X	0					X	1			X	10						100										
Ag 338.289 {100}	X						X				X						X		X									
Al 167.079 {501}	X	0									X	10					X	100										
Al 308.215 {109}	X																											
Al 396.152 { 85}	X																											
As 193.759 {474}	X	0									X	10			X	50	X	100										
As 197.262 {471}	X										X				X		X											
Ba 233.527 {445}	X	0					X	1	X	5	X	10	X	20	X	50	X	100										
Ba 455.403 { 74}	X						X		X		X		X		X		X											
Ba 493.409 { 68}	X										X						X											
Be 313.042 {108}	X	0	X	0.25	X	0.5	X	1	X	5	X	10				50	X	100										
Be 234.861 {144}	X														X		X											
Ca 315.887 {107}	X	0																100										
Ca 317.933 {106}	X																											
Ca 393.366 { 86}	X																											
Ca 396.847 { 85}	X																X											
Cd 226.502 {449}	X	0			X	0.5	X	1	X	5	X	10			X	50	X	100										
Cd 228.802 {447}	X				X		X		X		X				X		X											
Cd 228.802 {448}	X				X				X		X				X		X											
Co 228.616 {447}	X	0					X	1	X	5	X	10			X	50	X	100										
Co 238.892 {141}	X																											
Cr 205.560 {464}	X	0					X	1	X	5	X	10			X	50	X	100										
Cr 267.716 {126}	X						X				X				X		X											
Cu 224.700 {450}	X	0					X	1	X	5	X	10	X	20	X	50	X	100										
Cu 324.754 {104}	X																											
Cu 327.396 {103}	X														X		X											
Fe 234.349 {144}	X	0																										
Fe 239.562 {140}	X																											
Fe 259.940 {129}	X																											
Mg 202.582 {466}	X	0																100										
Mg 279.079 {121}	X																											
Mg 280.270 {120}	X																											
Mn 257.610 {131}	X	0							X	5	X	10	X	20	X	50	X	100										
Mn 259.373 {130}	X								X		X		X		X		X											
Mo 202.030 {466}	X	0							X	5	X	10	X	20	X	50	X	100										
Mo 203.844 {465}	X								X		X		X		X		X											
Mo 204.598 {464}	X								X		X		X		X		X											
Ni 221.647 {452}	X	0						1		5		10				50		100										
Ni 231.604 {445}	X						X		X		X				X		X											
Pb 216.999 {455}	X	0								5		10						100										
Pb 220.353 {453}	X								X		X						X											
Pb 220.353 {153}	X								X		X						X											
Sb 206.833 {463}	X	0								5		10		20		50		100										
Sb 217.581 {455}	X								X		X		X		X		X											

Table 4b. TAL list Concentrations/Ranges for ICP ug/L cont.

Element, Wavelength and Order	lStd9=1000		CalStd10=10000		CalStd12=100K		CalStd13=10000		CalStd14=50000		CalibStd15=100	
	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	
Ag 328.068 {103}	1000											
Ag 338.289 {100}												
Al 167.079 {501}	1000		10000				100000		500000		1e+006	
Al 308.215 {109}		X				X				X		
Al 396.152 { 85}		X						X				X
As 193.759 {474}	1000		10000									
As 197.262 {471}		X										
Ba 233.527 {445}	1000		10000									
Ba 455.403 { 74}		X										
Ba 493.409 { 68}		X										
Be 313.042 {108}	1000											
Be 234.861 {144}												
Ca 315.887 {107}	1000	X	10000			X	100000	X	500000	X	1e+006	
Ca 317.933 {106}		X						X		X		
Ca 393.366 { 86}												
Ca 396.847 { 85}		X										
Cd 226.502 {449}	1000											
Cd 228.802 {447}												
Cd 228.802 {448}												
Co 228.616 {447}	1000	X	10000									
Co 238.892 {141}		X										
Cr 205.560 {464}	1000	X	10000	X	100000							
Cr 267.716 {126}		X										
Cu 224.700 {450}	1000	X	10000		100000							
Cu 324.754 {104}		X		X								
Cu 327.396 {103}		X		X								
Fe 234.349 {144}	1000	X	10000			X	100000	X	500000	X	1e+006	
Fe 239.562 {140}		X				X		X		X		
Fe 259.940 {129}		X				X				X		
Mg 202.582 {466}	1000	X	10000			X	100000	X	500000	X	1e+006	
Mg 279.079 {121}		X				X		X		X		
Mg 280.270 {120}		X										
Mn 257.610 {131}	1000	X	10000		100000							
Mn 259.373 {130}		X		X								
Mo 202.030 {466}	1000		10000									
Mo 203.844 {465}												
Mo 204.598 {464}		X										
Ni 221.647 {452}	1000	X	10000									
Ni 231.604 {445}		X										
Pb 216.999 {455}	1000	X	10000	X	100000							
Pb 220.353 {453}												
Pb 220.353 {153}		X		X								
Sb 206.833 {463}	1000	X	10000									
Sb 217.581 {455}		X										

Table 4c. TAL list Concentrations/Ranges for ICP ug/L cont.

Element, Wavelength and Order	Calibration Standards																					
	Blank		CalStd1=0.25		CalStd2=0.5		CalStd3=1		CalStd4=5		CalStd5=10		CalStd6=20		CalStd7=50		CalStd8=100		Ce	
	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	
Se 196.090 {472}	☒	0	☐		☐		☐		☐		☒	10	☐		☒	50	☒	100	☒	
Se 206.279 {463}	☒		☐		☐		☐		☐		☐		☐		☐		☒		☒	
Tl 190.856 {476}	☒	0	☐		☐		☐		☐		☒	10	☐		☐		☒	100	☒	
Tl 190.856 {477}	☒		☐		☐		☐		☐		☒		☐		☐		☒		☒	
V 290.882 {116}	☒	0	☐		☐		☐		☐		☐	10	☐	20	☐	50	☒	100	☒	
V 292.402 {115}	☒		☐		☐		☐		☐		☒		☒		☒		☒		☒	
Zn 202.548 {466}	☒	0	☐		☐		☐		☐		☒	10	☐		☐		☒	100	☒	
Zn 206.200 {463}	☒		☐		☐		☐		☐		☒		☐		☐		☒		☒	
Zn 213.856 {457}	☒		☐		☐		☐		☐		☒		☐		☐		☒		☒	
Y 324.228 {104}*	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☐	
Y 371.030 { 91}*	☒		☐		☐		☐		☐		☐		☐		☐		☐		☐	
Y 224.306 {451}*	☒		☐		☐		☐		☐		☐		☐		☐		☐		☐	
Na 588.995 { 57}	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☒	
Si 251.611 {134}	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☒	
Ti 323.452 {104}	☒	0	☐		☐		☐		☒	5	☒	10	☐		☒	50	☒	100	☒	
Ti 334.941 {101}	☒		☐		☐		☐		☒		☒		☐		☒		☒		☒	
Sr 407.771 { 83}	☒	0	☐		☐		☒	1	☒	5	☒	10	☐		☐		☒	100	☒	
Sr 421.552 { 80}	☒		☐		☐		☒		☒		☒		☐		☐		☒		☒	
Sn 189.989 {477}	☒	0	☐		☐		☐		☐		☒	10	☐		☐		☒	100	☒	
B 249.678 {135}	☒	0	☐		☐		☐		☐		☒	10	☐		☐		☒	100	☒	
B 249.773 {135}	☒		☐		☐		☐		☐		☒		☐		☐		☒		☒	
Li 670.784 { 50}	☒	0	☐		☐		☐		☐		☒	10	☐		☐		☒	100	☒	
K 766.490 { 44}	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☒	
P 213.618 {457}	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☐	
S 182.034 {485}	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☒	
Hg 184.950 {482}	☒	0	☐		☐		☐		☐		☐		☐		☐		☒	100	☒	
Ce 404.076 { 83}	☒	0	☐		☐		☐		☐		☐		☐		☐		☐		☒	

Table 4d. TAL list Concentrations/Ranges for ICP ug/L cont.

Element, Wavelength and Order	alStd9=1000	CalStd10=10000		CalStd12=100K		CalStd13=10000		CalStd14=50000		CalibStd15=100	
	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc
Se 196.090 {472}	1000	☒	10000	☐		☐		☐		☐	
Se 206.279 {463}		☒		☐		☐		☐		☐	
Tl 190.856 {476}	1000	☒	10000	☐		☐		☐		☐	
Tl 190.856 {477}		☒		☐		☐		☐		☐	
V 290.882 {116}	1000	☒	10000	☐		☐		☐		☐	
V 292.402 {115}		☒		☐		☐		☐		☐	
Zn 202.548 {466}	1000	☒	10000	☒	100000	☐		☐		☐	
Zn 206.200 {463}		☒		☒		☐		☐		☐	
Zn 213.856 {457}		☐		☐		☐		☐		☐	
Y 324.228 {104}*		☐		☐		☐		☐		☐	
Y 371.030 { 91}*		☐		☐		☐		☐		☐	
Y 224.306 {451}*		☐		☐		☐		☐		☐	
Na 588.995 { 57}	1000	☒	10000	☐		☐		☐		☒	1e+006
Si 251.611 {134}	1000	☒	10000	☒	100000	☐		☐		☐	
Ti 323.452 {104}	1000	☒	10000	☐		☐		☐		☐	
Ti 334.941 {101}		☒		☐		☐		☐		☐	
Sr 407.771 { 83}	1000	☒	10000	☐		☐		☐		☐	
Sr 421.552 { 80}		☒		☐		☐		☐		☐	
Sn 189.989 {477}	1000	☒	10000	☐		☐		☐		☐	
B 249.678 {135}	1000	☒	10000	☐		☐		☐		☐	
B 249.773 {135}		☒		☐		☐		☐		☐	
Li 670.784 { 50}	1000	☒	10000	☐		☐		☐		☐	
K 766.490 { 44}	1000	☒	10000	☐		☐		☐		☒	1e+006
P 213.618 {457}		☒	10000	☐		☐		☐		☐	
S 182.034 {485}	1000	☒	10000	☐		☐		☐		☒	1e+006
Hg 184.950 {482}	1000	☐		☐		☐		☐		☐	
Ce 404.076 { 83}	1000	☐		☐		☐		☐		☐	

Note: These metals are calibrated using a blank and minimum of three standards. It is not allowable to remove any mid-levels to obtain an acceptable calibration; all points must be used. Multi-level calibrations must be sequential.

Appendix A.

Element specific standard prep for multipoint calibration of ICP.

A1 Calibration Standard 0.25 (Be, & Cd): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.25 ul of SPEX Quality Assurance l Standard 3 and 0.25 ul of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 0.25 ug/L.

A2 Calibration Standard 0.50 (Be & Cd): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 50uL of SPEX Quality Assurance Standard 3 and 50uL of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 0.50 ug/L.

A3 Calibration Standard 1.0 (Ag, Ba, Be, Cd, Co, Cr, Mn, Mo, Ni, Pb, Se, Sb, Tl, V, & Zn): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1 ml of conc. HNO3 and 1mL conc. HCl. Add 1.0 ul of SPEX Quality Assurance Standard 3 and 1.0 ul of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1 ug/L

A4 Calibration Standard 5.0 (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Sb, Tl, V, & Zn): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 5 ul of SPEX Quality Assurance Standard 3 and 5 ul of SPEX Quality Control Standard 21. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 5 ug/L

A5 Calibration Standard 10.0 (Ag, As, B Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Li, Mo, Ni, Pb, Se, Sb, Tl, V, Sr, Sn, Ti & Zn): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 10 ul of SPEX Quality Assurance Standard 3 and 10 ul of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10 ug/L

A6 Calibration Standard 20 (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe Mn, Mo, Ni, Pb, Sb, Tl, & V): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 20uL of SPEX Quality Assurance Standard 3 and 20uL of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 20 ug/L

A7 Calibration Standard 50 (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, Tl, V & Zn): Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 50uL of SPEX Quality Assurance Standard 3 and 50uL of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 50 ug/L

A8 Calibration Standard 100(Ag, As, B Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Li,Mo, Ni, Pb, Se, Sb, Tl, V, Sr, Sn, Ti & Zn (: Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 100 ul of SPEX Quality Assurance Standard 3 and 100 ul of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100 ug/L

A9 Calibration Standard 1000 (Ag, Al, As, Ba, Be, Ca, Cd Ce Co, Cr, Cu, Fe, Hg, K Mg, Mn, Mo, Ni, Na Pb, Se, Si, S Tl, V & Zn): Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1000uL of SPEX Quality Assurance Standard 3 and 1000uL of SPEX Quality Assurance Standard 23 and add 0.1 ml from single element standards 1000ug/mL Ce, Hg, K, Na Si and S . Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1000 ug/L

A10 Calibration Standard 10000(Ag, As, B Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Li, Mo, Ni, Pb, Se, Sb, Tl, V, Sr, Sn, Ti & Zn and add 1.0 ml from single element standards 1000ug/mL Ce, Hg, K, Na Si and S): Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 10000uL of SPEX Quality Assurance Standard 3 and 10000uL of SPEX Quality Assurance Standard 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10,000 ug/L

A11 Calibration Standard 100000 (Al, Ca, Fe, & Mg): Into a 100mL volumetric flask, add 5mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL of HCl. Add 1mL of 10,000 mg/L Al, 1mL of 10,000 mg/L Ca, 1mL of 10,000 mg/L Fe and 1mL of 10,000 mg/L Mg . Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100,000 ug/L Al, Ca, Fe, Mn, and Mg.

A12 Calibration Standard 100K (Cr, Cu, Mn, & Pb): Into a 100mL volumetric flask, add 5mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL of HCl and add 10 ml of Cr 1000 mg/L, 10 mls Cu 1000 mg/L, 10 mls Pb 1000 mg/L, 10 mls and 10 ml of Mn 1000 mg/L and mix by inverting several times. Transfer to a clean Nalgene bottle.

Prepare every 6 months or as needed. Concentration:100,000 ug/L , Cr, Cu, , Mn, and Pb.

A13 Calibration Standard 500000 (Al, Ca, Fe, & Mg): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL of HCl. Add 5mL of 10,000 mg/L Al, 5mL of 10,000 mg/L Ca, 5mL of 10,000 mg/L Fe and 5mL of 10,000 mg/L Mg. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500,000 ug/L Al, Ca, Fe and Mg

A14 Calibration Standard 1000000 (Al, Ca, Fe, K, Na, S & Mg): Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL of HCl. Add 10mL of 10,000 mg/L Al, 10mL of 10,000 mg/L Ca, 10mL of 10,000 mg/L Fe 10mL of 10,000 mg/L Mg, 10mls of 10,000 mg/L K, 10mls of 10,000 mg/L Na, and 10mls of 10,000 mg/L S. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1,000,000ug/L Al, Ca, Fe and Mg

A17 Calibration Blank: Into a 1 L. volumetric flask, add 750 mL of Milli-Q water and 10 mL of conc. HNO3 and 10mL HCl. Mix, dilute to volume with Milli-Q H2O. Transfer to a clean 1 L. Nalgene bottle. Prepare every 6 months or as needed.

A18 ICV/CCV: Into a 1000mL volumetric flask, add 10mL Milli-Q water, 1mL of conc. HNO3 and 10mL of conc. HCl. Add 10.0mL Spex Certiprep Spike Sample Standard 1 or equivalent and 2.0mL Interference A or equivalent, 0.5 mls of 1000 ug/L Mo, 0.5 mls of 1000ug/ L Si,0.5 mls 1000ug/ L Li, 0.5 mls of 1000ug/ L Sn. 0.5mls of 1000ug/ L Sr 1000ug/ L Ti and 0.5 mls 10000 ug/L standards Na, K, and S . Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentrations listed in LIMS.

A19 ICSAB: Into a 500mL volumetric flask, add 300mL Milli-Q water, 5mL of conc. HNO3 and 5mL of conc. HCl. Add 50 ml of SPEX Interferents A or equivalent, 15.0mLs of 10,000 mg/L Fe, 2.5mL Spex Certiprep QA 3 and 2.5 ml Spex Certiprep-QA 23 or equivalent. Dilute to volume with Milli-Q water and mix by inverting several times.

A20 ICSA (Al, Ca, Fe, Mg at 500 mg/L, and Ce, V at 10,000 ug/L) - Into a 500 mL volumetric flask, add 300 mL Milli-Q H2O, 5 mL conc. HNO3, and 5 mL conc. HCl. Add 50 mL of SPEX Interferents A or equivalent, 15.0 mL of Fe (10,000 mg/L), 5.0 mL Ce (1000 mg/L), and 5.0 mL V (1000 mg/L). Dilute to volume with Milli-Q H2O and mix by inverting several times.

A21 ICSA-1 (Mn at 10,000 ug/L) - Into a 500 mL volumetric flask, add 300 mL Milli-Q H2O, 5 mL conc. HNO3, and 5 mL conc. HCl. Add 5.0 mL Mn (1000 mg/L). Dilute

to volume with Milli-Q H2O and mix by inverting several times. of 1000 mg/L Ni. Dilute to volume with Milli-Q water and mix by inverting several times.

A22 ICSA-2 (Ba, Be, Sn at 10,000 ug/L) - Into a 500 mL volumetric flask, add 300 mL Milli-Q H2O, 5 mL conc. HNO3, and 5 mL conc. HCl. Add 5.0 mL Ba (1000 mg/L), 5.0 mL Be (1000 mg/L), and 5.0 mL Sn (1000 mg/L). Dilute to volume with Milli-Q H2O and mix by inverting several times.

A23 ICSA-3 (Cr, Cu, Co, Mo at 10,000 ug/L) - Into a 500 mL volumetric flask, add 300 mL Milli-Q H2O, 5 mL conc. HNO3, and 5 mL conc. HCl. Add 5.0 mL Cr (1000 mg/L), 5.0 mL Cu (1000 mg/L), 5.0 mL Co (1000 mg/L), and 5.0 mL Mo (1000 mg/L). Dilute to volume with Milli-Q H2O and mix by inverting several times.

A24 ICSA-4 (Ni, Ti at 10,000 ug/L) - Into a 500 mL volumetric flask, add 300 mL Milli-Q H2O, 5 mL conc. HNO3, and 5 mL conc. HCl. Add 5.0 mL Ni (1000 mg/L) and 5.0 mL Ti (1000 mg/L). Dilute to volume with Milli-Q H2O and mix by inverting several times.

Table 5. Sodium and Potassium Concentrations/Ranges for ICP (mg/L)

Element, Wavelength and Order	Calibration Standards																	
	Blank		CalibStd-0.5		CalibStd-1.0		CalibStd-5.0		CalibStd-10.0		CalibStd-50.0		CalibStd-100		CalibStd-200		CalibStd-500000	
	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc
K 766.490 (44)	☒	0	☒	0.5	☒	1	☒	5	☒	10	☒	50	☒	100	☒	200	☐	
Na 330.237 (102)	☒	0	☐	0.5	☐	1	☐	5	☐	10	☒	50	☒	100	☒	200	☐	
Na 589.592 (57)	☒		☒		☒		☒		☒		☐		☐		☐		☐	
Al 309.271 (109)	☒	0	☐		☐		☐		☐		☐		☐		☐		☒	500
Ca 317.933 (106)	☒	0	☐		☐		☐		☐		☐		☐		☐		☒	500
Fe 259.940 (130)	☒	0	☐		☐		☐		☐		☐		☐		☐		☒	500
Mg 279.079 (121)	☒	0	☐		☐		☐		☐		☐		☐		☐		☒	500
Y 360.073 (94)*	☒	0	☐		☐		☐		☐		☐		☐		☐		☐	

Note: These metals are calibrated using a blank and minimum of three standards. It is not allowable to remove any mid-levels to obtain an acceptable calibration; all points must be used. Multi-level calibrations must be sequential.

Appendix B

Standard Prep for Sodium and Potassium analysis.

B1 Calibration Standard 0.5: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 2mL of conc. HNO3 and 2mL conc. HCl. Add 0.05mL Sodium 1000mg/L and 0.05mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 0.5 mg/L Na, K.

B2 Calibration Standard 1.0: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.1mL Sodium 1000mg/L and 0.1mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1 mg/L Na, K.

B3. Calibration Standard 5.0: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.5mL Sodium 1000mg/L and 0.5mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 5 mg/L Na, K.

B4. Calibration Standard 10: Into a 100mL volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1mL Sodium 1000mg/L and 5mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10 mg/L Na, K.

B5. Calibration Standard 50: Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 5mL Sodium 1000mg/L and 5mL

Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 50 mg/L Na, K.

B6. Calibration Standard 100: Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 10mL Sodium 1000mg/L and 10mL Potassium 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100 mg/L Na, K.

B7. Calibration Standard 200: Into a 100mL volumetric flask, add H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 50mL Sodium 1000mg/L and 50mL Potassium 1000mg/L. Mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 mg/L Na, K.

B8. Calibration Standard 500 high std: Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 5mL Aluminum 10,000mg/L, 5mL, Calcium 10,000mg/L, 5mL, Magnesium 10,000mg/L and 5mL Iron 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 mg/L Al, Ca, Mg, and Fe.

B9. ICV/CCV: Into a 100mL volumetric flask, add 50mL Milli-Q water, 1mL of conc. HNO3 and 1mL of conc. HCl. Add 1.0mL 10,000mg/L Na and 1.0mL 10,000 K. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100 mg/L Na an K.

B8. ICSAB: Into a 100mL volumetric flask, add 10mL Milli-Q water, 1mL of conc. HNO3 and 1mL of conc. HCl. Add 10 ml of SPEX Interferents A or equivalent, 3.0mLs of 10,000 mg/L Fe, 1.0mL 10,000mg/L Na and 1.0mL 10,000 K. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100mg/L Na and K, 500,000ug/L Al, Ca, Fe and Mg.

Table 6. Boron and Silicon Concentrations/Ranges for ICP (ug/L)

Element, Wavelength and Order	Calibration Standards													
	Blank		CalibStd-50		CalibStd=50 &10		CalibStd=500 &1		CalibStd=1000&2		CalibStd=5000&1		CalibStd=500000	
	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc
B 249.773 {135}	☒	0	☒	50	☒	100	☒	1000	☒	2000	☒	10000	☐	
Si 251.611 {134}	☒	0	☐		☒	50	☒	500	☒	1000	☒	5000	☐	
Al 308.215 {109}	☒	0	☐		☐		☐		☐		☐		☒	500000
Ca 317.933 {106}	☒	0	☐		☐		☐		☐		☐		☒	500000
Fe 234.349 {144}	☒	0	☐		☐		☐		☐		☐		☒	500000
Mg 279.079 {121}	☒	0	☐		☐		☐		☐		☐		☒	500000
Y 360.073 {94}*	☒	0	☐		☐		☐		☐		☐		☐	

Note: Boron and Silicon are calibrated using a blank and a minimum three standards. It is not allowable to remove any mid-levels to obtain an acceptable calibration; all points must be used. Multi-level calibrations must be sequential.

Appendix C

Standard Prep for Boron and Silicon Analysis

C1. Calibration Standard 50 ug/L B: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.05 ml Spex Certiprep QA std. 23 or equivalent. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 50 ug/L B

C2. Calibration Standard 50 ug/L Si & 100 B ug/L: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 0.1 ml Spex Certiprep QA std. 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 50 ug/L Si & 100 ug/L B

C3. Calibration Standard 500 ug/L Si & 1000 B ug/L: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1.0 ml Spex Certiprep QA std. 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 ug/L Si &1000 ug/L B.

C4. Calibration Standard 1000 ug/L Si & 2000 B ug/L: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1.0 ml Spex Certiprep QA std. 23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration:1000 ug/L Si &5000 ug/L B.

C5. Calibration Standard 5000 ug/L Si & 10000 B ug/L: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 1.0 ml Spex Certiprep Q std23. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 5000 ug/L Si &10000 ug/L B.

C6. Calibration Standard 500 high std: Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 1mL of conc. HNO3 and 1mL conc. HCl. Add 5mL Aluminum 10,000mg/L, 5mL, Calcium 10,000mg/L, 5mL, Magnesium 10,000mg/L and 5mL Iron 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 mg/L Al, Ca, Mg, and Fe.

C7. ICV/CCV: Into a 100mL **plastic** volumetric flask, add 50mL of Milli-Q water, 1 mL of conc. HNO3 and 1mL conc. HCl. Add 0.1mL of 1000mg/L Boron and 0.1mL of 1000mg/L Silicon (alternate sources from calibration source). Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1000 ug/L Boron and Silicon.

C8. ICSAB: Into a 100mL volumetric flask, add 10mL Milli-Q water, 1mL of conc. HNO3 and 1mL of conc. HCl. Add 10 ml of SPEX Interferents A or equivalent, 3.0mLs of 10,000 mg/L Fe, 0.05 ml 1000 mg/L B and 0.5 ml 1000 mg /L Si. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 ug/L B and Si, 500,000 ug/L Al, Ca, Fe and Mg.

Table 7. Lithium, Tin, Strontium, and Titanium Concentrations/Ranges for ICP ug/L

Element, Wavelength and Order	Calibration Standards													
	Blank		1		10		100		1000		10000		500000	
	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc	?	Conc
Li 670.784 (50)	☒	0	☒	1	☒	10	☒	200	☒	1000	☒	10000	☐	
Sn 189.989 (477)	☒	0	☐		☐	10	☐	100	☐	1000	☒	10000	☐	
Sn 189.989 (478)	☒		☐		☐		☐		☐		☐		☐	
Sr 407.771 (83)	☒	0	☒	1	☒	10	☒	100	☒	1000	☐	10000	☐	
Sr 421.552 (80)	☒		☐		☐		☐		☐		☐		☐	
Ti 334.941 (101)	☒	0	☐	1	☒	10	☒	100	☒	1000	☒	10000	☐	
Ti 337.280 (100)	☒		☒		☐		☐		☐		☐		☐	
W 224.875 (450)	☒	0	☐		☒	10	☒	100	☒	1000	☒	10000	☐	
W 239.709 (141)	☒		☐		☐		☐		☐		☐		☐	
Al 309.271 (109)	☒	0	☐		☐		☐		☐		☐		☒	500000
Ca 317.933 (106)	☒	0	☐		☐		☐		☐		☐		☒	500000
Fe 259.940 (130)	☒	0	☐		☐		☐		☐		☐		☒	500000
Mg 279.553 (121)	☒	0	☐		☐		☐		☐		☐		☒	500000
Y 360.073 (94)*	☒	0	☐		☐		☐		☐		☐		☐	

Appendix D

Standard prep for Lithium, Tin, Titanium, Strontium, and Tungsten

D1. Calibration Standard 1: Into a 1000mLvolumetric flask, add 50mL of Milli-Q H2O, 10mL of conc. HNO3 and 10mL conc. HCl. Add 0.01 ml Spex Certiprep QA standard 23 or equivalent and 0.001 1000mg/L Sn. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1 ug/L

D2. Calibration Standard 10: Into a 1000mLvolumetric flask, add 50mL of Milli-Q H2O, 10mL of conc. HNO3 and 10mL conc. HCl. Add 0.1 ml Spex Certiprep QA std. 23 or equivalent and .01 1000mg/L Sn. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10 ug/L Li, Sr, Sn, and Ti.

D3. Calibration Standard 100: Into a 1000mLvolumetric flask, add 50mL of Milli-Q H2O, 10mL of conc. HNO3 and 10mL conc. HCl. Add 1.0 ml Spex Certiprep QA std. 23 or equivalent and 0.1 1000mg/L Sn. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 100 ug/L Li, Sr, Sn, and Ti.

D4. Calibration Standard 1000: Into a 1000mLvolumetric flask, add 50mL of Milli-Q H2O, 10mL of conc. HNO3 and 10mL conc. HCl. Add 10.0 ml Spex Certiprep 23 or equivalent and 1.0 1000mg/L Sn. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 1000 ug/L Li, Sr, Sn, and Ti.

D5. Calibration Standard 10000: Into a 1000mLvolumetric flask, add 50mL of Milli-Q H2O, 10mL of conc. HNO3 and 10mL conc. HCl. Add 100.0 ml Spex Certiprep QA std. 23 or equivalent and 10.0 1000mg/L Sn. Dilute to volume with Milli-Q H2O and

mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 10000 ug/L Li, Sr, Sn, and Ti.

D6. Calibration Standard 500000 high std: Into a 100mL volumetric flask, add 10mL of Milli-Q H2O, 10mL of conc. HNO3 and 10mL conc. HCl. Add 5mL Aluminum 10,000mg/L, 5mL, Calcium 10,000mg/L, 5mL, Magnesium 10,000mg/L and 5mL Iron 1000mg/L. Dilute to volume with Milli-Q H2O and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 mg/L Al, Ca, Mg, and Fe.

D7. ICV/CCV: Into a 1000mL volumetric flask, add 50mL of Milli-Q water, 10 ml of conc. HNO3 and 10mL conc. HCl. Add 0.5mL of 1000mg/L Li, 0.5mL of 1000ug/L Sn, 0.5mL of 1000ug/L Sr, 0.5 ml of 1000mg/L Silicon and 0.5 ml of 1000mg/L Titanium. (all alternate sources from calibration source). Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 ug/L Li, Sr, Sn, Ti, and W.

D8. ICSAB: Into a 100mL volumetric flask, add 10mL Milli-Q water, 1mL of conc. HNO3 and 1mL of conc. HCl. Add 10 ml of SPEX Interferents A or equivalent, 3.0mLs of 10,000 mg/L Fe, 0.05 ml of 1000 mg/L Sr, 0.05 ml 1000 mg /L of Li, 0.05 ml 1000 mg /L of Sn, 0.05 ml 1000 mg /L of Ti, 0.05 ml. Dilute to volume with Milli-Q water and mix by inverting several times. Transfer to a clean Nalgene bottle. Prepare every 6 months or as needed. Concentration: 500 ug/L Li, Sr, Sn, Ti, and W and 500,000ug/L Al, Ca, Fe and Mg.

Note: For DOD-QSM data the lowest level (Calib. Level # 1) on a multi-point curve is prepared at concentrations equal to or less than the MRL /LLOQ for any given project and these levels are subject to change.

FMT9-01 iCAP 6000/6500 Data Review Checklist (Example)

iCAP 6000 / 6500 Data Review Checklist	Analysis Date:		Data File:		Date of review:
Cal Std ID: LIMS # :	Analyst:		Reviewer:		Approved? Yes / No
Is Audit Trail turned on or Manual Manipulations addressed? Yes / No (If no, any manual manipulations must be initialed, dated, and reason(s) stated for change)					
QC Parameters : 6010 / 200.7 / QSM / Other	**YES**	**NO**	**YES**	**NO**	**Comments:**
1) Calibration linearity: r > 0.995 / r > 0.998					
2) ICV: 90-110% / 95-105%					
3) ICB: < 3X IDL / <LOD / <LOQ					
4) ICSA: < ABS LOD					
5) ICSAB: 80-120%					
6) MRL: 70-130% / 80-120%					
7) MDL Check: >LOD					
8) CCV1/CCB1 (CCV: 90-110%)					
9) CCV2/CCB2 (CCB: < 3X IDL / <LOD / <LOQ)					
10) CCV3/CCB3					
11) CCV4/CCB4					
12) CCV5/CCB5					
13) CCV6/CCB6					
Preparation Batch Parameters	**YES**	**NO**	**YES**	**NO**	
Prep Batch ID#:__________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD or ≤ ½ RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					
PDS: ±15% / 20% / 25% Sample#:____________					
Prep Batch ID#:__________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD or ≤ ½ RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					
PDS: ±15% / 20% / 25% Sample#:____________					
Prep Batch ID#:__________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD or ≤ ½ RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					
PDS: ±15% / 20% / 25% Sample#:____________					
Prep Batch ID#:__________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD or ≤ ½ RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					

Revision Number	Description of Changes	Date
02	Document changed to incorporated administrative requirements of ISO 17025 and QSM 5.0. Descriptions of changes have not been tracked in previous versions of this document.	03/12/2014
03	Added 4.2 QSM reference	3-9-2015
03	Added LDR and ICAL QC requirements to table 3	3-9-2015
04	Updated RSD requirement in section 12.3.1 from 5% to 3%.	03/02/2016
05	Added LLOQ standard reference at 6.2, 6.10,12.5.3,13.9, 13.10, 22.0 and D.8	4/11/17
5.1	Added frequency and criteria for spikes following EPA Method 200.7, Included WI 200.7 drinking water interference requirements.	09/15/17
5.2	Added ferric iron calculation (15.3). Updated LLCCV definition (6.4). Added LLCCV criteria to Table 3. Added Standard vendors (sec. 10.0). And added QSM 5.1 reference.	05/22/2018
5.3	Incorporated changes to ICSA solutions recommended by WI DNR. Changes made to sections 6.4, 12.4, 13.8, Table 3, and Appendix A.	4/16/2019

CT LABORATORIES

delivering more than data from your environmental analyses

STANDARD OPERATING PROCEDURE

MT 012 Mercury Cold Vapor Atomic Absorption (CV)

Review Date: 05/12/2018

05/24/2018

Technical Review by: Date

07/06/18

Approved by: Quality Assurance Date

Table of Contents

1. SCOPE OF APPLICABILITY

1.1. This method is appropriate for measuring mercury concentrations in groundwater, wastewater, drinking water, TCLP extracts, soils, sediments, and sludge-type materials.

2. SUMMARY OF METHOD

2.1. Prior to analysis, the samples must be prepared according to the procedures discussed in this Standard Operating Procedure (SOP).

2.2. This is a cold-vapor atomic absorption technique, based on the absorption of radiation at 254-nm 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. Absorbance (peak height) is measured as a function of mercury concentration.

3. DEFINITIONS

3.1. For full definitions on all terms applicable to this method, see the Quality Assurance Manual (QAM).

3.2. For a list of common acronyms and abbreviations, see QAM

3.3. Method Reporting Limit (MRL) or Contract Required Detection Limit (CRDL) Standard - Detection level standard at a level near but below the reporting limit, or at a level specified by client contract. When required, it is to be analyzed following the ICB, and prior to the last CCV standard in the run.

3.4. Serial Dilution Analysis (SD) - A sample is diluted 1:5 with method blank solution and analyzed. The diluted result and the undiluted result should agree within a limit of precision defined by the program (SW846, CLP, 200.7) or client QAPP. **For QSM work, a SD will be conducted at a minimum rate of one per prep batch per unique matrix upon the failure of the MS.**

4. HEALTH AND SAFETY

4.1. Gloves and protective clothing shall be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in

samples. All activities performed while following this procedure shall utilize appropriate laboratory safety systems.

5. INTERFERENCES

5.1. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

5.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

5.3. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL).

5.4. Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

5.5. This method allows for detection of small quantities of mercury. All potential sources of mercury contamination should be avoided. This would include sources of mercury present in other lab areas.

6. EQUIPMENT AND SUPPLIES

6.1. Hydra II Mercury Analyzer with ASX-500 autosampler

6.2. Argon gas, HP grade

6.3. 50 mL disposable centrifuge tubes and caps. (Fisher p/n 05-539-9 or equivalent)

6.4. 25 mL Class A volumetric pipettes

6.5. 100 mL volumetric flasks

6.6. 25 mL glass Class A, TD, graduated cylinders

6.7. 1, 2, 3, 4, 5 mL Class A volumetric pipettes

6.8. Eppendorf pipette, 0.100 to 1.000 mL range

6.9. Environmental Express Hot Blocks set at 90-95 ^{0}C

6.10. Thomas Cain DEENA Automated Sample Preparation Systems (DEENA I and DEENA II)

6.11. Balance: 0.01g capacity

6.12. Thermometer: For monitoring temperature of the block at beginning and end of digestion process.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric acid, H_2SO_4, concentrated: Trace metal grade (Fisher p/n A300C-212)

7.1.2. Nitric acid, HNO_3, concentrated: Trace metal grade (Fisher p/n A509-212 or equivalent)

7.1.3. Hydrochloric acid, HCl, concentrated: Trace metal grade (Fisher p/n A508SK212 or equivalent)

7.1.4. Potassium permanganate solution, 5% w/v: Prepared by dissolving 50 g Potassium Permanganate (Fisher p/n P279-212 or equivalent) in 1000 mL of DI water. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

7.1.5. Potassium persulfate solution, 5% w/v: Prepared by dissolving 50 g Potassium Persulfate (Fisher p/n P282-500 or equivalent) in 1000 mL of DI water. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

7.1.6. Sodium chloride-hydroxylamine sulfate solution, 12% w/v: Prepared by dissolving 60 g Sodium Chloride (Fisher p/n) and 60 g of Hydroxylamine Sulfate in 500 mL of DI water. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

7.1.7. Stannous chloride (10% $SnCl_2$ w/v in 7% HCl v/v): to a 1000 mL volumetric flask dissolve 100 g Stannous Chloride (VWR part number MK817604) in 70 mL concentrated HCl. Stir until $SnCl_2$ is completely dissolved. Additional heat may be necessary to get complete dissolution. Once dissolved, dilute to line and cool. Prepare as needed. Expires 6 months from date of preparation. Store at room temperature in metals lab.

7.1.8. Aqua regia: In a fume hood, carefully add three volumes of concentrated HCl to one volume of concentrated HNO_3. Prepare fresh daily.

7.2. Stock Standards

7.2.1. Mercury stock standards, 1000 mg/L certified solutions, two sources. One is to be used for the calibration standards and the other for the LCS. (Ultra-Scientific ICP-080 and JT Baker 6934-04 or equivalents). Store at room temperature in the metals lab. Expiration dates are given by the manufacturer.

7.3. Calibration Standards

7.3.1. Intermediate Stock #1 (10,000 µg/L) : To a 100 mL volumetric flask add 50 mL DI water and 0.2 mL concentrated HNO_3 and 0.2 mL HCl. Transfer 1.0 mL of 1000 mg/L Hg stock standard. Dilute to 100 mL with DI water and mix. Prepare fresh daily.

7.3.2. Intermediate Stock #2 (100 µg/L) :To a 100 mL volumetric flask add 50 mL DI water and 0.2 mL concentrated HNO_3 and 0.2 mL HCl. Transfer 1.0 mL of 10,000 µg/L intermediate stock #1. Dilute to 100 mL and mix. Prepare fresh daily.

7.3.3. Using 100 mL volumetric flasks, add 50 mL DI water and 0.2 mL concentrated HNO_3 and 0.2 mL concentrated HCl to each. Add the following volumes of 100 µg/L intermediate stock #2, dilute to volume with DI water, and mix well.

Standard Concentration (µg/L)	Volume (mL) of Intermediate Stock Std. #2 Added
0.5	0.5
1	1
2	2
4	4
5	5

Using a 25 mL volumetric pipette, transfer 25 mL of each to 50 mL centrifuge tubes. Add 25 mL reagent water to another centrifuge tube for the calibration blank.

7.3.4. ICV/LCS and CCV: (ICV/LCS from second source, CCV from same source as standards)

7.3.4.1. Intermediate Stock #1 (10,000 µg/L): To a 100 mL volumetric flask add 50 mL DI water and 0.2 mL concentrated HNO_3 and 0.2 mL HCl. Transfer 1.0 mL of 1000 mg/L Hg stock standard. Dilute to 100 mL and mix. Prepare fresh daily.

7.3.4.2. Intermediate Stock #2 (100 µg/L): To a 100 mL volumetric flask add 50 mL DI water and 0.2 mL concentrated HNO_3 and 0.2 mL HCl. Transfer 1.0 mL of 10,000 µg/L intermediate stock #1. Dilute to 100 mL and mix. Prepare fresh daily.

7.3.4.3. Check Standard/LCS: To a 100 mL volumetric flask add 50 mL DI and 0.2 mL concentrated HNO_3 and 0.2 mL HCl. Add 3.0 mL of the 100 µg/L intermediate stock from the second source standard, dilute to the line and mix.

7.3.4.4. Using a 25 mL volumetric pipette, transfer 25 mL of each to 50 mL centrifuge tubes.

7.3.4.4.1. Note: Due to different digestion matrices for aqueous and solid samples, two sets of standards must be prepped to match the matrix for each digestion

8. SAMPLE HANDLING AND PRESERVATION

8.1. Aqueous

8.1.1. Preserved with HNO_3, pH < 2

8.1.2. 28 Day Hold Time

8.2. Solids

8.2.1. Preserved in Refrigerator (4°C)

8.2.2. 28 Day Hold Time

9. PROCEDURE

9.1. *Manual Digestion:*

9.1.1. Turn on the Hot Block and allow it to heat to 95ºC while the samples are being prepared.

9.1.2. Sample Preparation-Aqueous:

9.1.2.1. Using a 25 mL graduated cylinder, transfer 25 mL of sample to a 50 mL polyethylene centrifuge tube. For drinking water analysis, a 25 mL Class A pipette must be used.

9.1.2.2. MS-MSD Prep: Add 0.50 mL of the 100 µg/L intermediate to a 25 mL final volume for a spike concentration of 2.0 µg/L (Table 1).

9.1.2.3. To each of the samples, MS-MSD, LCS, standards, and blanks add 1.25 mL concentrated H_2SO_4 and 0.625 mL concentrated HNO_3 under a hood.

9.1.2.4. To all samples, standards, and blanks add 3.75 mL Potassium permanganate ($KMnO_4$) solution.

9.1.2.5. Tightly cap the samples and mix by inverting several times.

9.1.2.6. The purple permanganate color should remain for at least 15 minutes. If it does not, add additional permanganate in 1 mL aliquots until the purple color remains for at least 15 minutes. Record any extra permanganate added on the mercury digestion bench sheet (Table 4). The same amount of extra permanganate will have to be added to all other samples and standards.

9.1.2.7. To all samples, standards, and blanks add 2.0 mL Potassium persulfate solution.

9.1.2.8. Place the samples and standards in the hot block. Heat at 90-95ºC for 2 hours. Record initial and final hot block temperatures on the mercury digestion bench sheet (Table 4).

9.1.2.9. Following digestion, remove the samples and place under a hood to cool. Alternately, the racks may be placed in a sink of cold water to hasten the cooling.

9.1.2.10. When the samples are cool, add 1.5 mL sodium chloride-hydroxylamine sulfate solution to all samples, standards, and blanks. Tightly cap and mix by inverting until samples are clear. Samples are now ready for analysis.

9.1.3. Sample Preparation-Solids:

9.1.3.1. Weigh triplicate 0.2 g (approximate) portions from separate areas of the sample container of the untreated sample into a 50 mL polyethylene centrifuge tube with a plastic spatula. Do not use metal spatulas. Record the weight on the mercury digestion bench sheet (Table 4). See the subsampling SOP FO-10 for further instructions on how to obtain a subsample for analysis.

9.1.3.2. Method Blank and LCS Prep: Weigh 0.50 g of Teflon boiling stones (Chemware, Item # 0919120 or equivalent) into each of two 50 mL polyethylene centrifuge tubes. For the LCS, add 0.5 mL of the 100 µg/L second source intermediate stock solution #2.

9.1.3.3. MS-MSD Prep: Add 0.50 mL of the 100 µg/L intermediate to a 25 mL final volume for a spike concentration of2.0 µg/L.

9.1.3.4. To all tubes, add 1.25 mL aqua regia reagent, and heat for 2 minutes in the hot block at 95ºC.

9.1.3.5. Cool, and then add 25 mL of DI water and 3.75 mL of Potassium Permanganate solution to each vial.

9.1.3.6. Tightly cap all vials and mix by inverting several times.

9.1.3.7. The purple permanganate color should remain for at least 15 minutes. If it does not, add additional permanganate in 1 mL aliquots until the purple color remains for at least 15 minutes.

Record any extra permanganate added on the mercury digestion bench sheet (Table 4). The same amount of extra permanganate must be added to all other samples and standards.

9.1.3.8. Place the samples and standards in the hot block. Heat at 90-95ºC for 30 minutes. Record initial and final hot block temperatures on the mercury digestion bench sheet (Table 4).

9.1.3.9. Cool, and then add 1.5 mL of Sodium Chloride-hydroxylamine sulfate to each sample and mix by inverting. The samples should turn clear.

9.1.3.10. If the digestate is clear and without solids distributed throughout the liquid portion, sample aliquots may be decanted for analysis. If not, then filtration will be necessary prior to analysis. Rinse a syringe filter (GF Syringe Filter, Part# SFGF025100MCU) with 2-3 ml of 10% HNO3 followed by 2-3 ml of DI H2O before filtering digestate. This filtration step may also be necessary for sample prepared using the Automated Digestion procedure (9.2).

9.2. *Automated Digestion (DEENA):*

9.2.1. See section 9.1.2.1-9.1.2.2 for measuring water samples.

9.2.2. See section 9.1.3.1-9.1.3.3 for weighing of solid samples.

9.2.3. Log-in to the computer associated to the DEENA automated sample preparation system.

9.2.4. Double-click on the DEENA shortcut icon on the desktop.

9.2.5. Next to “instrument selection”, select the sampler to be used. The program will open.

9.2.6. The blue light on the DEENA system will turn off, indicating that the computer is communicating with the instrument.

9.2.7. Prior to digesting samples, the automated digester needs to be calibrated. This is done before the first run of the day. See section 9.

9.2.8. Open up a template workspace. Click “file”, “new from”, “C-drive”, “program files”, “Thomas Cain”, “DEENA”. Choose the desired template for the method to be run.

9.2.9. Click the “automated mode” tab. The template that was chosen from the DEENA file is now loaded. The template will display the method steps, reagent list and tray setup.

9.2.10. Open the “method tab” and click the method to be run. Then click “ok”.

9.2.11. Click the “rack definition” tab. In the window, make sure start position is “1” and then fill in the number of samples to be digested. Click “ok” (figure 6).

9.2.12. Place the samples in the digestion block. Cover samples with reflux tray. Check to make sure all reagent bottles are at adequate level for analysis. Click “run” on the screen.

9.2.13. Upon completion, save the workspace run log to Q-drive, DEENA I and II, run log by the date followed by rl1 or rl2 (designating a run log which instrument was used).

9.2.14. Remove digestion tubes from the system. Make sure volume level of samples are accurate. Cap the digestion tubes. The samples are ready for analysis.

9.2.15. For detailed instructions for automated digestion, see the DEENA operator’s manual, rev.1.2.3.

9.3. Instrument Set-up:

9.3.1. Power up the M-6000A and autosampler and allow the instrument to warm up for one hour.

9.3.2. Turn on the lamp and gas supply and allow the lamp to warm up and the gas to flow for 15 minutes.

9.3.3. Place autosampler tubing into rinse water (1% HCl/1% HNO3)

9.3.4. Verify that the sample capillary (inlet insert) is 0.5 mm above the gas/liquid separator center post.

9.3.5. Open vents on waste container

9.3.6. Inspect peristaltic pump tubing for wear and flat spots and replace if necessary.

9.3.7. Place the peristaltic pump tubing in their appropriate holes and holder clips. Do not lock shoe clamps at this time.

9.3.8. Initiate M-6000A program by clicking on the M6000 icon, then controls, and finally the autosampler page.

9.3.9. Start the autosampler rinse pump by clicking the pump on and the probe down.

9.3.10. Place reagent capillary in a beaker of DI water and start the peristaltic pump in a clockwise rotation.

9.3.11. Lock down the peristaltic shoe clamps.

9.3.12. Inspect liquid flows. The GLS drain should be flowing smoothly with no build up or pulsing of liquid. The waste line from the peristaltic pump to the waste container should be liquid/gas with no vibration. If this is not the case upon inspection, stop immediately and change the GLS drain line and/or waste line.

9.3.13. Wet the GLS center post. Pinch the drain line prior to the tee of the peristaltic pump drain tubing. Let two or three liquid bubbles go to the top of the GLS center post and release the drain line. If the liquid does not bubble, fill the GLS to the top of the center post and release the drain line.

9.3.14. Attach GLS exhaust tube to the GLS.

9.3.15. Place reagent capillary in the reagent bottle.

9.3.16. Open the appropriate worksheet and verify that the gas flow of the worksheet matches what is listed in the controls, if the flow is not the same make the necessary change and click set gas.

9.3.17. Zero the M-6000A using the autozero. Autozero is located under Instrument Zero Instrument.

9.3.18. Peak profile the high standard and verify baseline and sample integration times. Do this by clicking on Analysis and then read then standard and then choose the highest standard. If there are any adjustments needed to the peak, refer to the M6000A software manual 5.6.12.

9.4. Analysis:

9.4.1. Insert sample labels by clicking on labels and then entering the sample ID numbers.

9.4.2. Right click to enter the QC standards after all the samples are entered. Choose “QC standard” for the CCV and “QC blank for the CCB.

9.4.3. Click on Analysis and then Click on start.

9.4.4. Choose the appropriate box and then click OK.

9.4.5. After analysis, click on file and choose return to main index.

9.4.6. Choose reports.

9.4.7. Click on the data tab and choose the data that you want to report.

9.4.8. Click on the Reports tab.

9.4.9. Click on Write test to file and then enter the LIMS run number and make sure it is saved in the Cetac folder on the I drive.

9.5. Shutdown:

9.5.1. Place the reagent capillary in a beaker of 10% nitric acid and cap the reagent bottle. Rinse the system for a minimum of ten minutes.

9.5.2. Place the reagent capillary in a beaker of DI water and rinse the system for one minute.

9.5.3. Raise sample probe by clicking on controls then autosampler and click probe up and pump off.

9.5.4. Remove reagent capillary from DI water.

9.5.5. Allow the drain and waste lines to run completely dry.

9.5.6. Turn off peristaltic pump.

9.5.7. Release peristaltic shoe clamps and release the pump tubing from their holder clips.

9.5.8. Close vents on waste container.

9.5.9. Remove GLS exhaust line from GLS.

9.5.10. Turn off gas and lamp.

9.5.11. Exit software and run off the autosampler and instrument.

10. CALCULATIONS AND DATA ANALYSIS AND REDUCTION

Liquid Concentration (µg/L) = A x C

$$\textit{Solid Concentrations (mg/kg)} = \frac{A \times B \times C}{D \times E}$$

A = instrument reading for sample (µg/L)
B = total volume of digestion (L)
C= analyst dilution factor (ex. For a 1 to 10 dilution, C = 10)
D = amount of sample used in digestion (g)
E = percent solids/100, if necessary

$$\textit{Spike Recovery (\%)} = \frac{\text{(Spiked sample concentration – Sample concentration)} \times 100}{\text{(Spike amount)}}$$

$$\textit{\%RSD} = \frac{(MS - MSD) \times 100}{(MS + MSD)/2}$$

MS = Matrix spike concentration
MSD = Matrix spike duplicate concentration

11. CALIBRATION AND STANDARDIZATION

11.1. *DEENA Calibration:*

11.1.1. Prior to digesting any samples using the automated sample digester, the system needs to be calibrated.

11.1.2. After logging into the DEENA system (refer to sections 9.2.3-9.2.6), click on the “manual mode” tab at the top of the screen.

11.1.3. Click the “pump calibration” tab (table 5).

11.1.4. Weigh out 5 digestion tubes and record their weights in the “initial weight” column for the 5 tubes.

11.1.5. Click “Go All”. The digester is dispensing water into the 5 empty tubes.

11.1.6. The tubes are then weighed again and the final weight is recorded in the “final weight” column.

11.1.7. The difference between the final weight and the initial weight is the amount of volume dispensed per “X” steps on the peristaltic pump. An average is then taken between the 5 replicates. The digester is now calibrated.

11.2. *Hot Block Calibration:*

11.2.1. Please refer to the Hot Block operator manual for instrument temperature calibration.

11.3. *Hydra II Calibration:*

11.3.1. The Hydra II Mercury Analyzer is calibrated before each use. Accuracy of the standards is verified by use of a second source standard.

11.3.2. In the upper window menu bar select Instrument, then calibrate. Enter the calibration information, which consists of the standard number and standard concentration in µg/L, and then press continue. The calibration data will now be available for sample analysis.

11.3.3. Calibration is done by injecting standards. In the calibration window under the methods tab, the minimum correlation coefficient can be set to ensure sample analysis is not wasted with a failing curve.

11.3.4. After all calibration points have been analyzed, the data system will prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

11.3.5. Quality control standards and calibration standards are treated the same as samples within the system.

11.3.6. Report only samples with raw results less than or equal to the highest calibration standard. Samples exceeding the highest standard’s concentration must be diluted and reanalyzed.

12. QUALITY CONTROL

12.1. Personnel operating the CVAA shall have background knowledge of the scientific principles used during this application. All operators shall perform an initial demonstration of capability (IDC) prior to analyzing any samples. It is preferable for the operator to have at least two semesters of college chemistry.

12.2. This SOP is designed to follow a variety of different projects and programs requirements. Table 2 is designed to illustrate the control steps and provisions required to adequately producing acceptable data.

12.3. Contract Specific Sample Analysis: For certain samples, limits are specified by the Quality Assurance Project Plan (QAPP) associated with a given project. For these samples follow the limits specified in the QAPP for that project.

13. DATA ASSESSMENT/ACCEPTANCE CRITERIA FOR QC MEASURES

13.1. When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. The analyst will review the data to ensure QC is acceptable and that exceedances are addressed. Acceptable data is then captured into the LIMS system.

13.2. All manual integrations will be reviewed for validity (See QA-016 for specifics).

13.3. After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness by filling out the checklist (Table 3) for data review guidance.

13.4. Once the analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

13.5. After the second reviewer approves the data, the reviewer sends the data to “validated” status in LIMS.

13.6. A paper hard copy of the data is then filed or archived. The package includes the checklist and data.

14. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

14.1. See QAM.

15. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

15.1. See QAM.

16. DATA RECORDS MANAGEMENT

16.1. Records are stored for a minimum of 5 years in accordance with the Quality Manual.

16.2. See SOP QA 003 for specifics on document control.

17. WASTE MANAGEMENT

17.1. Samples are routinely held for up to six weeks from analysis date before they enter the waste stream. Waste disposal of samples and standards follows the procedures documented in the Laboratory Waste Disposal SOP (Quality Assurance Section, SOP NO. FO-8, Rev. 4).

18. REFERENCES

18.1. Test Methods for Evaluating Solid Waste, EPA, SW-846, Methods 7470A, 7471B.

18.2. Methods for the Determination of Metals in Environmental Samples. EPA/600/R94/111, Method 245.1

18.3. See CT Laboratories Quality System Manual, Section 8 for general references.

18.4. CT Laboratories Quality Manual, current revision.

18.5. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 4.2, October 2010.

18.6. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.0, July 2013 or most recent revision.

18.7. National Environmental Laboratory Accreditation Conference (NELAC), 2003 NELAC Standard Chapters 1 to 6, EPA/600/R-04/003, June 5, 2003 or most recent version.

18.8. ISO. 2005. General requirements for the competence of testing and calibration laboratories. ISO17025.

18.9. Thomas Cain, DEENA Operation Manual, Revision 1.2.3, November 2015

18.10. Atomic Absorption Methods, SW846, Method 7000A, Revision 1, July 1992

18.11. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.1, January 2017 or most recent revision.

19. Appendices

Table 1. Mercury Spike Prep

COLD VAPOR Element	Spike Amt. mL	Spike Solution Supplier	Stock Conc. µg/L	Final Vol. mL	Expected Conc. µg/L
Hg	0.50	Ultra 1000 mg/L	100.0	25.0	2.0

Table 2. Standard Quality Control Requirements and Corrective Action

QC Type	**Frequency**	**Conc. Level**	*Acceptance Criteria*	*Corrective Action*
ICal	Each time the instrument is set up. The ICal consists of five standards and a blank.	0 + 0.5 – 5.0 µg/L	Correlation coefficient of .995 or greater DOD-QSM: $r^2 \geq 0.99$.	Terminate analysis, correct problem and recalibrate.
ICV	Immediately after the ICal	3 µg/L	Second source standard, SDWA: 95-105% SW846:90-110% DOD-QSM: 90-110%	Reanalyze once, if still unacceptable terminate analysis, correct problem and recalibrate
ICB	Immediately after the ICV	0	Routine work: < MDL, 5% of the Reg. Limit or 5% of the sample concentration. DOD-QSM: < LOD	Reanalyze once, if still unacceptable terminate analysis, correct problem and recalibrate.
LCS	1 per batch of ≤ 20 samples per matrix per day	mid cal. Range	SDWA; 85-115% SW846; 80-120% DOD-QSM: See QSM Appendix C	Reanalyze once, if still unacceptable terminate analysis, correct problem and reanalyze all associated samples.

CCV	After every 10th sample and at the end of the analytical sequence	mid cal range	SDWA; 90-110% SW846; 90-110% ACOE- see client QAPP DOD-QSM: 90-110%	Reanalyze once, if still unacceptable recalibrate and reanalyze all samples back to the last acceptable CCV or ICV..
CCB	Immediately following each CCV	0	Routine work: < MDL, 5% of the Reg. Limit or 5% of the sample concentration. ACOE: ½ the MRL DOD-QSM: < LOD	Reanalyze once, if still unacceptable reanalyze all samples back to the last acceptable CCB or appropriately qualify results.
MS-MSD or MS-DUP (QSM)	5% of samples per matrix per day 10% of samples per matrix per day as per method 245.1	See Figure 1.	% Rec. 80-120 Applicable when spike level is >25% of original analyte level in the sample and RPD ≤ ± 20% 7470A-1 In-house limits if more stringent than Method Default of 80-120%, 7471B-1 In-house limits if more stringent than Method Default of 75-125%, 245.1 In-house limits if more stringent than Method Default of 70-130%, or as specified in DOD-QSM or QAPP	Perform PDS
Post Digestion Spike (PDS)	Upon failure of MS or per batch for ACOE work	Same level as MS	85-115% DOD-QSM: 80-120%	Qualify data as matrix interference or perform MSA

Method Blank	1 per batch of 20 samples	0	Routine work: < MDL, 5% of the Reg. Limit or 5% of the sample concentration. DOD-QSM: < 1/2 LOQ or < 1/10th amount in samples or < 1/10th regulatory limit, whichever's highest	Investigate and isolate possible source and correct problem; then reanalyze all associated samples, if possible, or qualify data (B)

Table 3. CVAA Checklist FMT11,12-01 (Example)

GFAA / FLAA / CVAA Data Review checklist		Method: 200.9		7000 series AA	245.1 & 245.2 245.7 7470a / 7471a
Instrumentation:	THERMO M SERIES AA				CETAC Hg ANALYZER
Analysis Date:	Data File:		Date Review:		**Analyte:**____________
Cal Std ID: LIMS # :	Analyst:		Reviewer:		Approved? Yes No
Is Audit Trail turned on or Manual Manipulations addressed? Yes / No (If no, any manual manipulations must be initialed, dated, and reason(s) stated for change)					
Calibration Parameters -	**YES**	**NO**	**YES**	**NO**	**Comments:**
1) Calibration linearity - r > 0.995					
2) ICV: 90-110% 95-105%					
2) ICVLL: 70-130% 80-120%					
3) ICB: <IDL / <LOD / <LOQ / <½ RL					
6) MRL: 70-130%					
7) CCV1/CCB1- (CCV: 90-110% / 80-120%)					
8) CCV2/CCB2 (CCB: <IDL / <LOD / <LOQ / <½ RL)					
9) CCV3/CCB3					
10) CCV4/CCB4					
11) CCV5/CCB5					
Preparation Batch Parameters	**YES**	**NO**	**YES**	**NO**	
Prep Batch ID#:________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD / <2.2X LOD / ≤ ½RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					
d)____________ matrix = ________					
e)____________ matrix = ________					
PDS: ±15% / 20% / 25% Sample#__________					
MSA Performed? Yes No					
Prep Batch ID#:________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD / <2.2X LOD / ≤ ½RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					
d)____________ matrix = ________					
e)____________ matrix = ________					
PDS: ±15% / 20% / 25% Sample#__________					
MSA Performed? Yes No					
Prep Batch ID#:________ Dig. Meth.__________					
LCS - generated limits or project specific limits					
MB - <LOD / <2.2X LOD / ≤ ½RL					
Spiked samples in batch:					
a)____________ matrix = ________					
b)____________ matrix = ________					
c)____________ matrix = ________					
d)____________ matrix = ________					
e)____________ matrix = ________					
PDS: ±15% / 20% / 25% Sample#__________					
MSA Performed? Yes No					FORM #: FMT11,12-01

FORM #: FMT11,12-01
Rev. #: 2.0
Effective Date: 08/19/2014
Page 1 of 1

Table 4. FMT12-03(Example)
Mercury Digestion Bench Sheet

FMT12-03

Mercury Digestion Bench Sheet

(Prep Methods 7470A & 7471A)

CCV ID: _____
ICV/LCSW ID: _____

*Matrix: _____
Balance ID: _____

Prep Batch #:	
Prep Method:	
Analyst:	
Date:	
Start Time:	

7470A= Hg Liquids
7471A= Hg Solids

End Date: _____
End Time: _____

Digestion Tube Lot #: _____
Block Used: _____
Cell Position for Temp. Check: _____
Initial-DigestionTemp (ºC): _____
Final-Digestion Temp (ºC): _____
Additional KMnO4 added (ml): _____
Aqua Regia added (ml) _____
Calibration Stds: _____

Reagent:	Ref. #
HNO3:	
H2SO4:	
NaCl/Hydrox.SO4:	
KMnO4:	
K2S2O8:	
Aqua-Regia:	

	Sample ID			(Solids) Sample Weight (g)	(Liquids) Sample Volume (ml)	Final Volume (ml)
		(MB)				25
		(LCS)				25
						25
		Comments:				25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
						25
		(DUP) if applicable				25
		(MS)	Parent Sample			25
		(MSD)				25
Leave >>		(DUP) if applicable				25
blank		(MS)	Parent Sample			25
		(MSD)				25
		(DUP) if applicable				25
		(MS)	Parent Sample			25
if N/A		(MSD)				25

MB=Method Blank, LCS=Laboratory Control Sample, DUP=Duplicate, MS=Matrix Spike & MSD=Matrix Spike Duplicate
*Matrix: Soil, Sludge, Waste, GW=Groundwater, WW=Wastewater, Tissue, TLCP, SPLP, ASTM or other.

A:	Spike Amount (ml)	Spike Conc. (ug/L)	Spike Ref. #

B:	Spike Amount (ml)	Spike Conc. (ug/L)	Spike Ref. #

Reviewed By/Date: _____

Hg Prep Template_FMT12-03 03/02/201509:39

Table 5: Calibration Window for DEENA

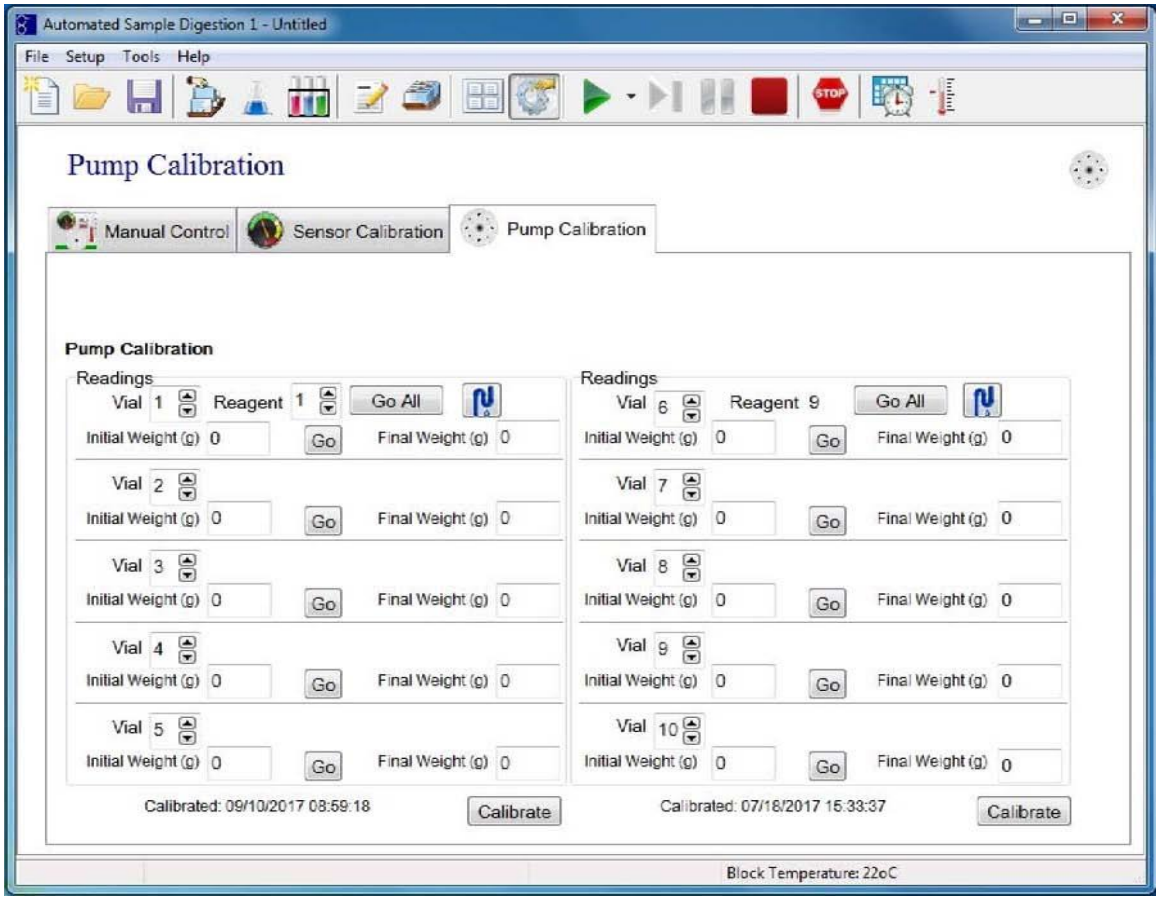


Table 6: Digestion Method Window for DEENA (Example)

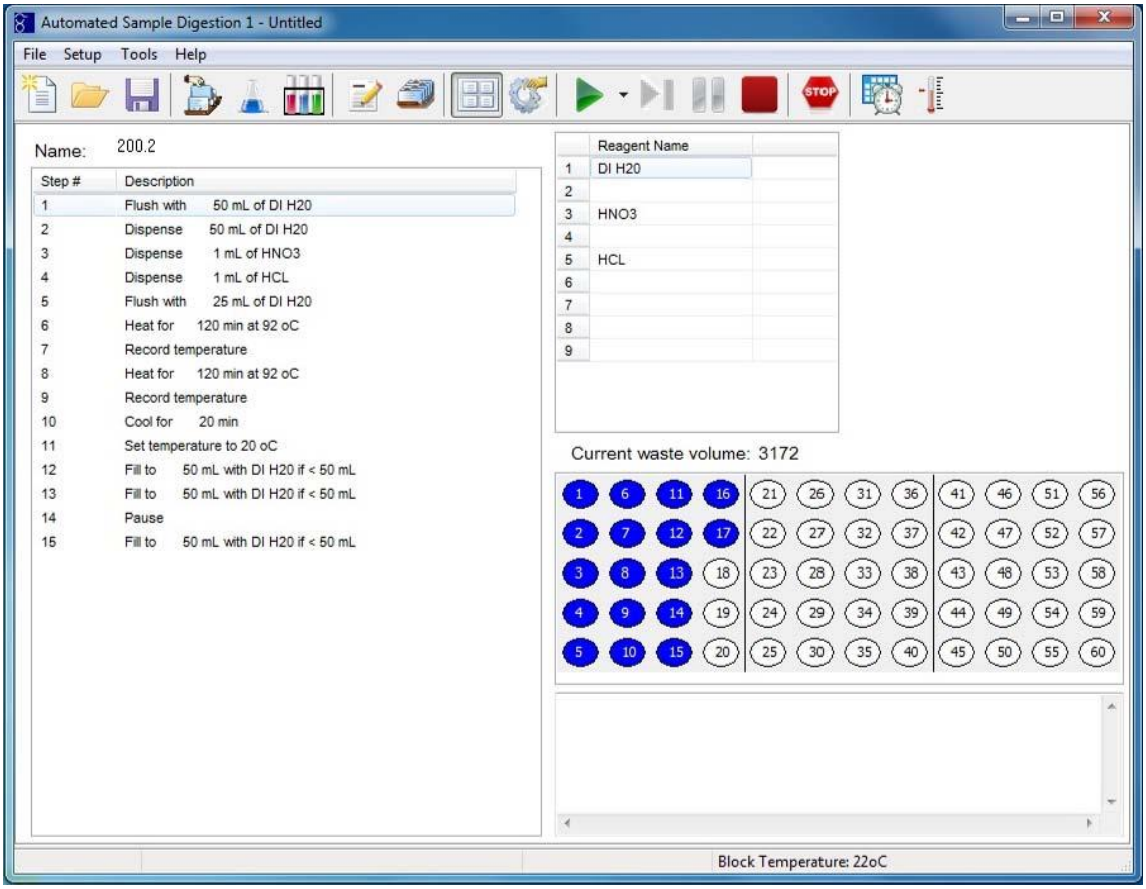
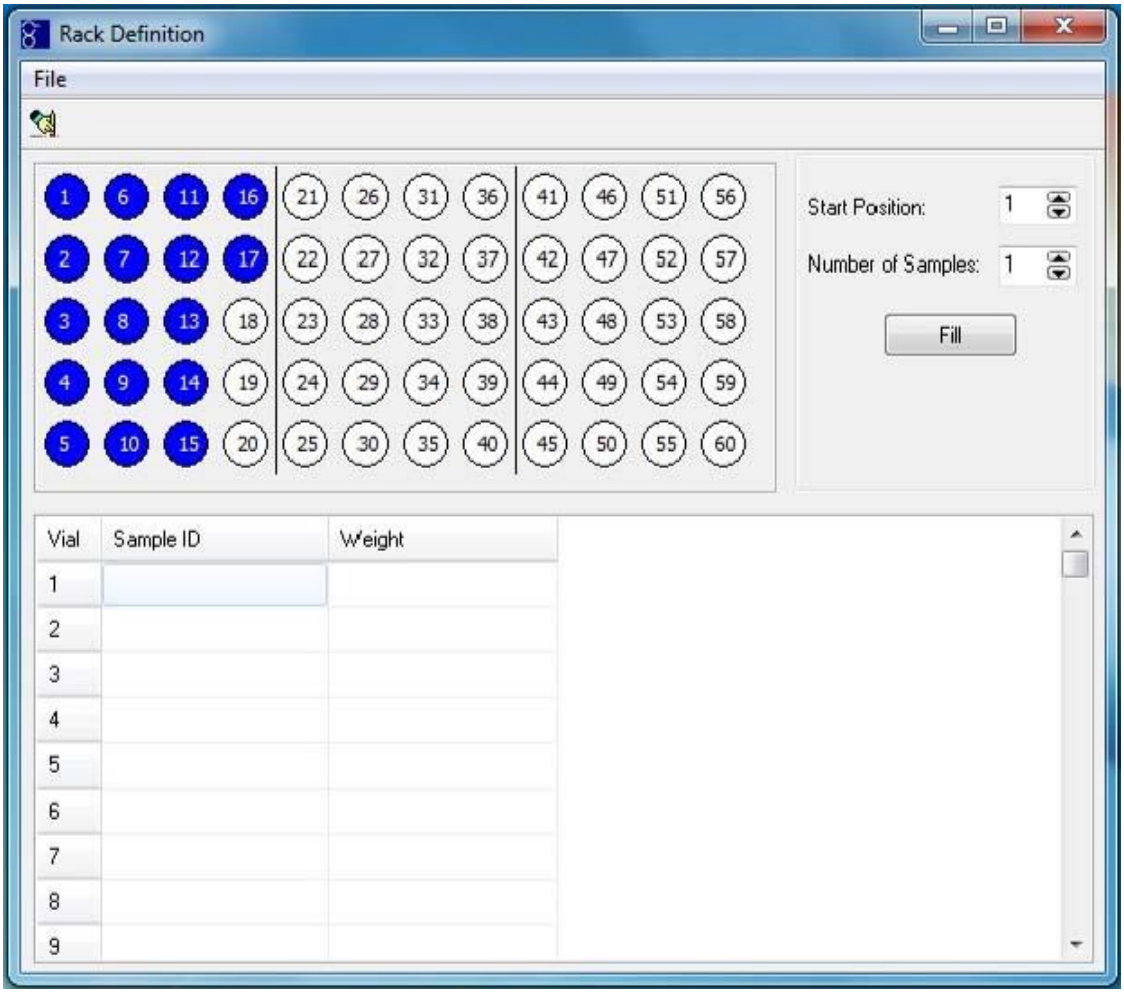


Table 7: Digestion Rack Window for DEENA



Revision Number	Description of Changes	Date
08	Document changed to incorporated administrative requirements of ISO/IEC 17025:2005 and QSM 5.0. Descriptions of changes have not been tracked in previous versions of this document.	03/14/2014
09	Update LCS and MS/MSD limits in Table 2 to meet method 245.1 criteria. And Included SW 846, Method 7000 reference to this SOP.	03/02/2016
10	Included DEENA Automated Digester Procedure	09/19/2017
10.1	Updated Table 2 to include Methods 7470A & 7471B MS/MSD recovery requirements Corrected MS/MSD criterea on Table 2. Added QSM 5.1 reference. Added filtration step (sec. 9.1.3.10) and use of Teflon beads for soil matrix	05/24/18

STANDARD OPERATING PROCEDURE
SV 004 Polychlorinated biphenyls (PCBs) as Aroclors by GC

Review Date: 08/08/2019

08/08/2019

Technical Review by: Date

08/08/2019

Approved by: Quality Assurance Date

Table of Contents

1.0 Identification of Test Method

This method is designed to follow procedures and QC requirements found in EPA SW-846 methods 3510, 3535, 3546, 3580 8000 and 8082 in order to determine quantities of semi-volatile organic compounds found in a variety of different sample matrices.

2.0 Applicable Matrix or Matrices

Semi-Volatile organic compounds are quantitated from a variety of matrices. This method is applicable to nearly all types of samples regardless of water content, including ground water, surface water, wastewater, waste oils, soils and sediments, as well as other matrices noted in SW-846 method 8082A.

3.0 Detection Limits

Method detection limits (MDLs) are determined annually and results vary from compound to compound. Water MDLs typically fall in the range of 0.020 to 0.20 ug/L. Soil MDLs are usually found to be between 2.0 to 16 ug/kg. Procedures for conducting MDL studies can be found in CT Laboratories Initial Method Performance and Reporting SOP Q23.

4.0 Scope and Application, including components to be analyzed

This method is used to quantify Semi-Volatile Polychlorinated Biphenyl's as aroclors in many types of solid waste matrices, soils, and groundwater. See Table 1.0 for typical target analyte list (TAL).

Table 1.0
Aroclor List

Aroclor Name
1016
1221
1232
1242
1248
1254
1260
1262
1268

5.0 Method Summary

5.1 This method describes procedures for isolating organic compounds through sample preparation from aqueous and soil matrices (reference methods SW846-3510, 3535, 3580 and 3546), concentration techniques that are suitable for preparing the extract, and the quantitative/ qualitative analysis for the determination of Polychlorinated Biphenyl's by method SW846-8082A.

5.2 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method applies for aqueous samples extracted by liquid-liquid separatory funnel (SW846-3510) or solid phase extraction (SW846-3535). Method applies for soil/sediment, and solid waste samples extracted by standard solvent extraction methods using microwave energy to produce

elevated temperature and pressure conditions in a closed vessel containing extraction solvent (SW846-3546). This method includes the extraction for waste oil samples using SW846-3580.

5.3 The resultant extract is chemically dried and concentrated using a TurboVap system and/or Kuderna-Danish (K-D) apparatus in preparation for instrumental analysis.

5.4 Extracts for PCB analysis can be subjected to a variety of cleanup steps, depending on the nature of the matrix interferences and target analytes. Suggested cleanup methods include; sulfur cleanup (Method 3660) (attachment I), Florisil (Method 3620) (attachment II), and Gel-Permeation Chromatography (GPC) cleanup (Method 3640A) (GPC SOP Rev. 0). Alternative cleanup methods (refer to SW-846) are; alumina (Method 3610) and silica gel (Method 3630). After cleanup, the extract is analyzed by injecting a known aliquot into a gas chromatograph equipped with dual capillary columns and ECD detectors.

5.5 The procedures contained within this method are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results.

6.0 Definitions

6.1 Solid Phase Extraction (SPE): The separation ability of solid phase extraction is based on the preferential affinity of desired or undesired solutes in a liquid, mobile phase for a solid, stationary phase through which the sample is passed. Impurities in the sample are either washed away while the analyte of interest is retained on the stationary phase, or vice-versa. Analytes that are retained on the stationary phase can then be eluted from the solid phase extraction cartridge with the appropriate solvent.

6.2 For full definitions on all terms applicable to this method, see Section 25.6 in the Quality Assurance Manual (QAM).

6.3 For a list of common acronyms and abbreviations, see QAM front matter.

7.0 Interferences

7.1 Solvents, reagents, glassware, and other sample processing hardware can yield artifacts and /or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Refer to each method for specific guidance on quality control procedures.

7.2 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

7.3 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, can cause degradation of certain analytes.

7.4 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interference, further cleanup of the sample will be necessary.

7.5 Elemental sulfur (S_8) is readily extracted from soil samples. High concentrations of sulfur will

cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through cleanup procedures such as Method 3660.

8.0 Safety

8.1 Gloves and protective clothing shall be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure must utilize appropriate laboratory safety systems.

8.2 The toxicity and carcinogenicity of the chemicals used in this method are not precisely defined. Each chemical and sample shall be treated as a potential health hazard, so care must be taken to prevent undue or extensive exposure.

9.0 Equipment and Supplies

9.1 Gas Chromatograph- An analytical system complete with gas chromatograph (HP 6890) suitable for split-splitless injection and all required accessories including syringes, analytical columns, electron capture detectors, auto sampler, electronic pressure control, and EZ Chrom Elite (3.3.2 SP1) data acquiring system.

9.1.1 Carrier gas: Hydrogen at 37.0 psi at 12 mls/min
Mode: Ramped Flow
Injection Volume: 1 ul
Injector: 250 °C with Restek Septa 27142
Mode: Pulse Split
Pulse Pressure: 37.0 psi
Pulse Time: 0.20 min.
Split ratio: 1.0.
Total Flow: 77.7 ml/min

Initial Flow – 17.6 ml/min (hold 1.00 min)
Ramp – 2.50 ml/minute
Final – 19 ml/min (hold for 0.0 minutes)
Ramp – 3.2 ml/min
Final – 27 ml/min (hold for 2.0 minutes)

Detector (s): 300 °C
Mode: Constant Makeup
Make-up Gas: Nitrogen at 40 mL/min.
Range: 2 on A and 3 B channel

Oven: Initial – 185 °C (hold for 0.4 minute)
Ramp – 10.10 °C/minute
Final - 192 °C (hold for 0.0 minutes)
Ramp – 13 °C/minute
Final - 220 °C (hold for 0.0 minutes)
Ramp – 30°C/minute
Final - 300 °C (hold for 0.0 minutes)

Note: Instrument operating parameters are subject to change to improve overall chromatography

(changes are noted in the Instrument Maintenance Log Book).

9.2 Analytical column pair:

9.2.1 30m x 0.32 mm ID bonded with 5% phenyl polysiloxane / 95% dimethylsiloxane, 0.25 um. (ZB-5, part # 7HM-G002-11 or equivalent).

9.2.2 30m x 0.32 mm ID bonded with 14% Cyanopropylphenyl/86% dimethylplysiloxane, 0.25 um (ZB-1701, part # 7HM-G006-11 or equivalent).

9.3 Water bath- heated and capable of accepting a Kuderna-Danish apparatus. (GlasCol 6 position heating mantel 100DRX30424 or equivalent)

9.4 CEM Microwave Accelerated Reaction System (MARS Xpress) extraction unit with Synergyprep software.

9.4.1 The CEM Mars extraction cycle:

Method 1
8-16 samples
Power: 100% at 800 watts
Ramp Time: 15 min
Pressure:0
Temp:110 C
Hold Time: 15 min

Method 2
17-48 samples
Power: 100% at 1600 watts
Ramp Time: 15 min
Pressure:0
Temp:110 C
Hold Time: 15 m

9.5 Organomation Nitrogen blow down concentrator (N-Evap).

9.6 TurboVap tubes: (Zymark 45817 or equivalent)

9.7 TurboVap; autoconcentrator

Temp: 45ºC
Pressure: 8-10psi

9.8 Analytical balance capable of accurately weighing to the nearest 0.01 gram (Fischer Scientific XD 2200 or equivalent).

9.9 Oven, muffle and drying.

9.10 Separatory funnel - 2000 mL Nalgene 4301, Teflon FEF lined with Teflon TFE stopcocks and

Tefzel ETFE screw closures (MG Scientific #F847-2L or equivalent).

9.11 2-Platform shakers (Eberbach Model 6010 150 V shaker, or equivalent) fitted with trays to hold 6 Nalgene separatory funnels each.

9.12 Kuderna-Danish (K-D) apparatus:

9.12.1 Concentrator tube, 10.0 mL, graduated. (Fisher # K570051-1025).
9.12.2 Evaporation flask- 500 mL or 250 ml (Fisher # K570035-0250).
9.12.3 Synder column- Three-ball macro (Fisher # K503000-0121).
9.12.4 Teflon clamps to attach concentrator tube to evaporation.

9.13 Graduated cylinder (Class A TC) - 1000 mL. (Fisher 08-559G).

9.14 Beaker - 250 mL and 600 mL.

9.15 Vials - 2.0mL (National Scientific – C4000) 12mL (Kimble #60815-1965), and 60 mL screw cap vials with Teflon lined caps (C&G #LX64-A030-A01A) or equivalents.

9.16 Pasteur Pipets; 5 ¾" and 9" (VWR #14672-200 and -300).

9.17 Funnels – glass. (VWR #154-08 or equivalent).

9.18 Volumetric flask – (Class A TC) 10, 25, 50, and 100 mL.

9.19 Syringes 10 uL, 100 uL, 500 uL, and 1,000 uL. (Hamilton or equivalent).

9.20 Boiling chips, carborundum, approximately 10/40 mesh (methylene chloride rinsed) (Fisher #09-191-12) equivalent.

9.21 Filter- Glass Microfiber 12.5 cm (Ahlstrom, MG # F136-1250).

9.22 CEM-MARS Microwave extraction tubes with plugs and caps, 75mL (CEM #574127)

9.23 Spatulas- stainless steel. (VWR #57952-253 or equivalent)

9.24 pH indicator paper- pH 0-14. (Whatman #2613991) or equivalent. Stored in general lab storage area.

9.25 Aluminum foil.

9.26 Solid Phase Extraction Unit (SPEU). 3 station manifold assembly (47mm). (UCT: ECUCTVAC347) or equivalent.

10.0 Reagents and Materials

10.1 Deionized water (Milli-Q processed), analyte free or equivalent.

10.2 Sodium sulfate (granular, anhydrous 60/120 mesh, JT Baker # 3375-05) or equivalent. If sodium sulfate passes in house lot check, it can be used as is and stored in air tight glass jar.

Otherwise condition sodium sulfate by heating to 400°C for 4 hours in a shallow glass tray loosely covered with foil and recheck for purity. Sodium sulfate will be stored in airtight glass jars and used within five years of opening or before the manufacturer's expiration date.

10.3 Silica sand- hydrocarbon free. Purify by heating to 400°C for 4 hours in a shallow glass tray, loosely covered with foil. Silica sand will be stored in airtight glass jars and used within five years of purifying.

10.4 Methylene chloride, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date. Or stored in large carboy tank provided by manufacturer and used within one year of opening or by the manufacturer's expiration date.

10.5 Acetone, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date.

10.6 Hexane, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date

10.7 Hydrogen (99.995% purity or greater).

10.8 Nitrogen (99.995% purity or greater)

10.9 Sulfuric Acid-1:1(v/v). ACS grade.Used within six months of mixing or before manufacturer's expiration date for any reagent used.

10.10 Sodium Hydroxide- 10N. ACS grade. Used within six months of mixing or before manufacturers expiration date for any reagent used.

10.11 Diatomaceous earth (Celite 545 – EMD #CX0574) or equivalent. Used within five years of opening or before the manufacturers expiration date.

11.0 Sample Collection, Preservation & Storage

11.1 Aqueous samples are collected in 1-L amber glass containers with Teflon lined lids. Aqueous samples are to be collected in duplicate. Solid samples are collected in 250-mL wide mouth glass containers with Teflon-lined lids. All samples are preserved by cooling to 4ºC. Soil samples must be extracted within 14 days and water samples must be extracted within 7 days from the date of collection.

11.2 Sample extracts are stored under refrigeration and analyzed within 40 days of extraction.

11.3 All soil samples are weighed on the top loading balance which is connected to a computer so that all weights can be automatically entered onto an Excel spread sheet. The spreadsheets are saved so the data can be transferred electronically to the LIMS system.

12.0 Quality Control

This SOP is designed to follow a variety of different projects and programs requirements. Table 3 is designed to illustrate the control steps and provisions required to adequately produce acceptable data.

13.0 Calibration and Standardization

13.1 Preparation of standards is documented in the Pest/PCB standards logbook. Each standard is labeled with a unique standard number to allow for tracking. Stock standards, once opened, expire in one year or sooner if routine QC indicates a problem, and are not to exceed the manufacturer's expiration date. Stock standards are saved in a capped vial in the original box in the freezer. Intermediate Stock Standards and Working Standards, which are subsequent dilutions made from the opened stock standard vial, expire in six months and are not to exceed the opened date of the stock standard or the manufacturer's expiration date.

13.2 Stock Standards -Stock Standards are purchased from vendors who provide certified solutions. Standards are stored at -10ºC in a freezer reserved for standard solutions. Unopened standards shall have the manufactures suggested expiration date. Stock standards, once opened, expire within six months and are not to exceed the manufacturer's expiration date. The following list of stock standards are certified, commercially prepared standards, such as:

Aroclor 1016/1260: Restek Part # 32039 at 1000 ug/mL.
Aroclor 1016: Restek Part # 32006 at 1000 ug/ml.
Aroclor 1221: Restek Part # 32007 at 1000 ug/ml.
Aroclor 1232: Restek Part # 32008 at 1000 ug/ml.
Aroclor 1242: Restek Part # 32009 at 1000 ug/ml.
Aroclor 1248: Restek Part # 32010 at 1000 ug/ml.
Aroclor 1254: Restek Part # 32011 at 1000 ug/ml.
Aroclor 1260: Restek Part # 32012 at 1000 ug/ml.
Aroclor 1262: Restek Part # 32409 at 1000 ug/ml.
Aroclor 1268: Restek Part # 32410 at 1000 ug/ml.
Surrogate Mix: Restek Part # 32000 at 200 ug/ml.

13.3 Intermediate Working Stock Standards: The Aroclor intermediate standards are prepared at an optimum level from the preparation of the working stock standard. Each Aroclor with surrogate are prepared at an optimum level for the intermediate stock standard. The concentration of each Aroclor is 10 ug/ml with surrogate concentrations of 0.5 ug/ml in hexane. The following is a list of each Aroclor.

Aroclor 1016	Aroclor 1254
Aroclor 1221	Aroclor 1260
Aroclor 1232	Aroclor 1262
Aroclor 1242	Aroclor 1268

Table 2.0
Intermediate Working Stock Standard Concentration

Intermediate Standard	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	1000	0.100	10.0	10.0
Surrogate	200	0.025	10.0	0.5

13.4 Calibration standards: PCB are to be determined as Aroclors, external calibration techniques will be used. An initial calibration is performed using a minimum of a five point calibration curve for Aroclors 1016/1260. These standard mixes will include many of the peaks represented in the other Aroclor mixtures. Standards for the other Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor (CF) for that specified Aroclor. The single-point calibration standard level is marked with an asterisk. In situations where only a few Aroclors are of interest for a specific project or program, the analyst will employ a minimum of a five point initial calibration of each of the Aroclors of interest. Alternative standard concentrations for the calibration curve can be prepared to meet client's or program's specified criteria.

Table 2.1
Calibration Points for the Aroclor(s) Linearity

Linearity Points	Spike Concentration (ug/ml) Aroclor(s)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml) Aroclor(s)	Final Concentration (ug/ml) Surrogate
1	10.0	0.030	10.0	0.03	0.0015
2	10.0	0.050	10.0	0.10	0.0025
3	10.0	0.200	10.0	0.20	0.010
4*	10.0	0.500	10.0	0.50	0.025
5	10.0	1.000	10.0	1.00	0.050
6	10.0	1.200	10.0	1.20	0.060

13.5 Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of Aroclors 1016/1260 at a concentration of 0.5 ug/ml each time the initial calibration is performed. These are made by taking known aliquots of the ICV intermediate standard and diluting them to volume in hexane. If the analyst uses a project specified Aroclor in Section 7.4, then the analyst must verify that Aroclor with an ICV.

Table 2.2
ICV Working Standard

Working ICV Standard	Intermediate Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	10.0	0.500	10.0	0.500
Surrogate	0.5	0.500	10.0	0.025

13.6 Continuing Calibration Verification Standard (CCV): A working standard solution for Aroclor 1016/1260 at a concentration of 0.5 ug/ml is used to check the validity of a calibration curve on a daily basis. If the analyst uses a project specified Aroclor in Section 7.4, then the analyst must use that Aroclor as the CCV. The variance of the Aroclor 1016/1260 mixture shall not be more than +/- 20% difference when compared to the mean calibration factor.

Table 2.3
CCV Working Standard

Working CCV Standard(s)	Intermediate Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	10.0	0.500	10.0	0.500
Surrogate	0.5	0.500	10.0	0.025

13.7 Surrogate standard: A commercially prepared certified solution of 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl is diluted in acetone to produce a working surrogate solution of 0.50 ug/mL. 0.5 mL is added to each sample and QC. The surrogate concentration is normalized to 100% from the spiking solution in the initial calibration. This will provide percent recoveries that transfer directly to LIMS.

Table 2.4
Surrogate Spiking Solution

Surrogate Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Surrogate	200	0.250	100.0	0.500

13.8 Spiking standards (matrix and control samples): Prepare a spiking solution in acetone that contains Aroclor 1016/1260 at a concentration of 10.0 ug/mL for water and sediment /soil samples. 0.5 ml is added to quality control and matrix spike samples. If client request a specified Aroclor, a spiking solution will be altered to match the Aroclor of interest

Table 2.5
Aroclor Spiking Solution

Aroclor Spiking Solution	Stock Standard Concentration (ug/ml)	Standard Volume (ml)	Final Volume (ml)	Final Concentration (ug/ml)
Aroclor(s)	1000.0	0.500	50.0	10.00

13.9 The initial calibration for SW-846-8082 chromatographic method involves the analysis of standards containing the target compounds at a minimum of five different concentrations covering the working range of the instrument across two dissimilar analytical columns. Each column must meet the initial calibration and continuing calibration criteria found in Table 3. In situations where only a few Aroclors are of interest for a specific project, the analyst will employ a multi-point initial calibration of each of the Aroclors of interest (e.g. five standards of Aroclor 1232 if this Aroclor is of concern and linear calibration models are employed) and not use the 1016/1260 mixture or the pattern recognition standards.

13.10 Quantitation is based upon indicator peaks in the Aroclor 1016/1260 mixture that are generally present in the Aroclors. The calibration factors (CF), and generated Aroclors 1016/1260 from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean calibration factor, the standard deviation (SD), and the relative

standard deviation (RSD) for each Aroclor peak. When the Aroclors 1016/1260 mixture is used to demonstrate detector response, the calibration model (linear or non-linear models) chosen for this mixture must be applied to the other Aroclors for which only standards are analyzed. A minimum of five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate the linearity.

Note: When selecting peaks for calibration, it is important to determine that common single-component pesticides such as DDT, DDD and DDE does not elute at the same retention time as the target peak.

13.11 The single point calibration standard will use a minimum of three to five peaks for each Aroclor. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of thee to five peaks are included and at least one peak that is unique to that Aroclor. The single standard for each of the other Aroclors will generate at least three calibration factors, one from each peak.

13.12 The identification of multi-peaked analytes such as PCBs as Aroclors can be performed by a combination of pattern recognition and retention time. Retention time windows are crucial to the identification of target compounds. Compare the retention time of each analyte in the calibration standard with the absolute retention time windows established in accordance with Method 8000 Section 11.6. Make three injections of target analyte standards over a course of 72-hour period. Each retention time must be to three decimal places. Calculate the mean and standard deviation of the target analytes. The width is 3x the standard deviation of the mean absolute retention time during the 72 hour period or 0.03 minutes, which ever is higher. If the standard deviation is 0.000, the laboratory will include more data points or use the default value of 0.01 minutes. Each analyte in each standard must fall within its respective retention time window. The retention time shall be set using the midpoint standard of the initial calibration curve or the value in the continuing calibration verification standard at the beginning of the analytical shift. If the analytes fall outside the established retention time window, the gas chromatographic system must either be adjusted so that a second analysis of the standard results in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

13.13 Prepare the Aroclor 1016/1260 calibration standards (in table 1.2) at a minimum of five different concentrations by adding known volumes of the intermediate stock standard to a volumetric flask and diluting to volume with hexane. Note: QSM requires that the LOQ or the lowest point in the curve, which ever is greater, be used for the reporting limit.

13.14 The lowest concentration calibration standard that is analyzed during an initial calibration curve, establishes the method's quantitation limit based on the final volume of the sample extract described in the preparative method or employed by the laboratory.

13.15 External standard calibration involves comparison of instrument response from the target compounds in the calibration standards. Sample peak areas are compared to peak areas of the standards. The ratio of the detector response to the amount of analyte in the calibration standard is defined as the calibration factor (CF). Aroclors are a multi-component standard. For the initial calibration curve, five peaks (or more) will be selected from each Aroclor 1016/1260 and calibrated using the average percent RSD of the peaks. If multi-point

calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate the linearity.

13.16 Linear calibration using the average calibration or response factor. When calculating, both calibration factors and response factors are a measure of the slope of the calibration relationship and assume that the curve passed through the origin. If the relative standard deviation (RSD) is less than or equal to 20%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin

13.17 Linear calibration using a least squared regression. When the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. The approach is to employ a regression equation that does not pass through the origin. This approach can also be employed based on past experience of the instrument response.

13.18 Non-linear calibration. When using a calibration model for quantitation, the curve must be continuous, continuously differentiable, and monotonic over the calibration range. The statistical considerations in using a non-linear calibration model require more data than the traditional linear approaches. A quadratic (second order) model requires the use of six initial calibration points.

13.19 Directly inject the prepared calibration standards into the gas chromatograph. An external calibration technique is employed. One of the external standards will be at a concentration near, but above the method detection limit. If the RSD $\leq$ 20%, the correlation of $r \geq 0.995$, or $r^2 \geq 0.990$ is obtained then the calibration is deemed acceptable.

13.20 Check the validity of the calibration by analyzing an ICV. The variance of any given compound shall not be more than +/- 20% difference. This standard must be run prior to sample analysis. If the percent drift or the percent difference criteria is not met, then the subsequent sample analysis for that analyte is not acceptable.

13.21 Continuous checking of the validity of the calibration by analyzing CCVs. The variance of any given compound shall not be more than +/- 20% difference. This standard must be ran at the beginning, every 20 samples or every 12-hour interval (which ever comes first), and at the end of the analysis run.

13.22 It is highly recommended to employ two standards (CCVs) at different concentrations to verify the calibration curve using non-linear calibration. One standard shall be near the quantitation limit or action limit. The choice of specific standards and concentrations is generally a method or project specific consideration.

13.23 When determining Polychlorinated Biphenyls by the external standard technique, calculate the calibration factor (CF) for each peak in each of the initial calibration standards using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in Nanograms)}}$$

13.24 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. This involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each multi-component peak.

$$\text{Mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

$$SD = \sqrt{\left(\frac{\sum_{I=1}^{n} (CF_I - \overline{CF})^2}{n-1}\right)}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

13.25 Linear Calibration: If the RSD of the calibration factor is greater than 20% over the calibration range, then linearity though the origin cannot be assumed. If this is the case, the analyst can employ a regression equation that does not pass through the origin. This approach can also be employed based on the past experience of the instrument response. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = mx + b$$

y = instrument response (peak area or height)
m = Slope of the line
x = Concentration of the calibration standard
b = The intercept

13.26 The analyst will not force the line through the origin, but have the intercept calculated from the five data points. The use of linear regression will not be used as a rationale for reporting results below the calibration range.

13.26.1 A linear least squares regression attempts to construct a linear equation of the form: y= mx + b, by minimizing the differences between the observed results (y_i, the response calculated from the constructed equation). The regression equation is:

$$y_i' = ax_i + b$$

where:

a = Regression coefficient or the slope of the line
b = The y-intercept
y_i' = Predicted (or calculated) response for the i^{th} calibration standard.
x_i = Mass of analyte in the i^{th} calibration standard aliquot

introduced into the instrument.

The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n} (y_i - y_i')^2$$

where n is the total number of calibration points. The regression calculations attempt to minimize the sum of squares, hence the name "least squares regression."

13.27 Weighting the sum of the squares of the differences can significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n} w_i \ (y_i - y_i')^2$$

where:

w_i = Weighting factor for the calibration standard (w=1 for unweighted least squares regression.
y_i = Observed instrument response (area or height) for the i^{th} calibration standard.
y_i' = Predicted (or calculated) response for the i^{th} calibration standard.
n = Total number of calibration standards.

13.28 Least Squares Equation (LSQ) weighting method to be used for calculation of least squares regression fits, either 1/x or $1/x^2$, gives increased importance to smaller concentrations and areas. LSQ weight can be applied to linear, quadratic, and cubic fits only.

13.29 Non-Linear Calibration: In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model can be employed. When using a calibration model for quantitation, the curve must be continuous, continuously differentiable, and monotonic over the calibration range. The model chosen shall have no more than four parameters, i.e., if the model is polynomial, it will be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

13.30 The statistical considerations in developing a non-linear calibration model require more data that the more traditional linear approaches described above. Linear regression employ five calibration standards for the linear model, a quadratic model requires a minimum of six calibration standards.

13.31 The "goodness of fit" of the polynomial equation is evaluated by calculating the weighed coefficient of the determination (COD);

$$n \qquad \_\_ \qquad n\text{-}1 \qquad n$$

$$COD = \frac{\sum_{i=1}^{n} (y_{obs} - y)^2 - \left(\frac{\text{------}}{n-p} \right) \sum_{i=1}^{n} (y_{obs} - Y_i)^2}{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2}$$

.

y_{obs} = Observed response (area) for each concentration from each calibration standard.

$\bar{y}$ = Mean observed response from the initial calibration
Y_I = Calculated response at each concentration from the initial calibrations.
n = Total number of calibration points (6 points for quadratic equation)
p = Number of adjustable parameters in the polynomial.

13.32 Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

14.0 Procedure

14.1 Water Extraction (Method SW-846, 3510)

14.1.1 Pre-rinse all glassware to be used in the extraction with methylene chloride (Pesticide Grade).

14.1.2 Mark the meniscus on the bottle for later determination of sample volume. (Refer to section 11.1) From the glass sample collection bottle, quantitatively transfer sample into a 2 liter separatory funnel.

14.1.3 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. Prepare each by adding one liter of Milli-Q water to 2 liter separatory funnels.

14.1.4 One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). In order of preference:

14.1.4.1 Select the sample where two full volume extra matrix was provided; use the extra volume supplied for a full volume MS and MSD.

14.1.4.2 Select a sample where one extra sample bottle was provided; quantitatively transfer half of the extra sample into a 2 liter separatory funnel and label MS. Transfer the other half of the sample into another 2 liter separatory funnel and label MSD.

14.1.4.3 Select a sample where no extra sample was provided and split it into three equal portions, one for the parent sample, one for the MS, and one for the MSD.

14.1.4.4For the last two situations concerning sacrificing a sample volume versus the inability to run a MS/MSD contact the project manager for proper procedure.

14.1.5 Add 0.5 mL of the surrogate standard mix to all samples by using a 0.5 ml syringe. In addition, add 0.5 mL of the proper spiking solution to the MS/MSD and LCS.

14.1.5.1 Surrogate and/or spike shall be added directly to the sample jar.

14.1.5.2 Reseal the sample jar and gently shake sample to mix.

14.1.5.3 If it is necessary to prepare split MS/MSD samples, the samples shall be quantitatively split using graduated cylinders and spiking shall occur directly into the graduated cylinder. Swirl gently to mix.

14.1.5.4 From the sample jar (or graduated cylinder), quantitatively transfer the sample into a 2-liter separatory funnel.

14.1.5.5 Check and adjust the extraction pH to between 5 and 9 with 10N sodium hydroxide and/or 1:1 sulfuric acid solutions.

14.1.5.6 Add 60 mL of methylene chloride to the sample jar (or graduated cylinder) and swirl to rinse sides of vessel. Transfer methylene chloride into the separatory funnel as well.

14.1.6 The sample is extracted by the automated shaker. Shake the samples vigorously for two minutes.

14.1.7 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. Decant the lower layer into a 250 ml beaker. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and will include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

14.1.8 Repeat the extraction two more times using a fresh 60 mL portion of methylene chloride.

14.1.9 Determine the original sample volume by filling the sample bottle to the mark with water and transferring it to a “Class A TC” 1 liter graduated cylinder for measurement. Note all sample volumes on the extraction bench sheet (see Tables 5 and 6).

14.1.10 Record all lot numbers, prepping analyst, times and dates on prep bench sheet (see Tables 5 and 6).

14.1.11 Samples can potentially require cleanup prior to concentration/analysis. Refer to attachments I and II or the GPC SOP (Rev. 0) for sample cleanup procedure.

14.1.12 Refer to section 14.4 for sample concentration.

14.2 Soil Extraction (Method SW-846, 3546)

14.2.2 Microwave extraction

14.2.2.1 Preparing the extraction tubes for use: extraction tubes, caps and plugs are washed in the dishwasher, rinsed with methanol and baked in 110 C oven for 1 hour. After they have cooled, rinse the extraction cell (tubes, plugs and caps) with methylene chloride.

14.2.2.2 Decant and discard any water layer from sediment sample. Mix sample thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks.

14.2.2.3 Dry sediment/soil and dry waste samples amenable to grinding: Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make the sample more amenable to grinding. Dry samples as much as possible, as water will cause un-even heating of the tubes.

14.2.2.4 Gummy, fibrous, or oily materials not amenable to grinding, shall be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make the sample easier to mix. Wipe samples can be placed directly into the cell.

14.2.2.5 Weigh approximately 10.0 g of sample to the nearest 0.01 g in a 250-mL beaker and record the final weight on prep bench sheet (See FSV4-02). Add 2.5 g of diatomaceous earth to the sample. Mix well. The samples shall be a free flowing powder. If sample is not free flowing, add more diatomaceous earth and/or sodium sulfate until the sample has a dry texture. This powder is mixed so that it will allow the sample to pass through a 1 mm sieve.

14.2.2.6 Transfer the ground sample in a 75 mL extraction cell. There should be a minimum head space of 25%.

14.2.2.7 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. Prepare by adding 10.0 g of sand and 2.5g of diatomaceous earth to a clean 250 ml beaker. Transfer sample to extraction cell.

14.2.2.8 One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). Select the sample and transfer approximately 40 grams to a 250 ml beaker. Mix well. Weigh two individual 10.0 grams aliquots of sample. Add drying agent. Transfer each sample aliquot to separate extraction cells. If there is no sample available to perform a matrix spike/matrix spike duplicate, contact project management. Default QC is a laboratory control spike duplicate.

14.2.2.9 Add 0.5 mL of the surrogate standard mix to all samples by using a 0.5 mL syringe. In addition, add 0.5 mL PCB spiking solution to the matrix

spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate).

14.2.2.10 Add 20 ml of (1:1) methylene chloride: acetone extraction solution to each tube. Insert tube plug and attach the cap to the extractor cell, making sure the cap is straight, screw on and torque with wrench**.** Shake each tube for 10 seconds to ensure the soil is mixed with the extraction solvent.

14.2.2.11 Place the extractor tube on the carousel in the appropriate slots for the number of tubes being used. Less than 16 use inside ring, greater than 16, use the outside ring then fill the inside ring. Schedule CEM Mars and begin the cycle. (Note: There must be a minimum of 8 samples, if less, use sand/solvent blanks to make up the shortage.)

14.2.2.12 Record all lot numbers, prepping analyst, times and dates on prep bench sheet (see FSV4-02).

14.2.2.13 Samples can potentially require cleanup prior to concentration/analysis. Refer to attachments I and II or GPC SOP (Rev. 0) for sample cleanup procedure.

14.2.2.14 Samples need to be shaken for 10 seconds to ensure sample residue is removed from tube wall prior to being poured out for concentration. Refer to section 14.4 for sample concentration.

14.3 Waste Dilution Extraction (SW846-3580)

14.3.1 (Refer to SOP FO-10 for subsampling guidance). Samples consisting of multiphase separations.

14.3.2 Pre-rinse “Class A TC” 10 ml volumetric with hexane.

14.3.3 One method blank and laboratory control spike must be prepared with each batch of 20 samples or less. One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD). If adequate sample is unavailable for a MS/MSD, contact project management for proper procedure.

14.3.4 Place the 10 ml volumetric on analytical balance (capable of accurately recording weight to the 0.001 g). Using a Pasteur pipet, transfer 1.0 g (to the nearest 0.001 g) to the volumetric. Record the weight.

14.3.5 Fill the volumetric half way with hexane.

14.3.6 Add 0.5 mL of the surrogate standard mix to all samples by using a 0.5 ml syringe. In addition, add 0.5 mL of the Aroclor 1016/1260 spiking solution to the matrix spike/matrix spike duplicate and laboratory control spike (laboratory control spike duplicate).

14.3.7 Bring samples up to volume with hexane. Transfer sample to a appropriately labeled 12 mL amber vial and cap. If samples are not analyzed immediately, store the sample extract in a refrigerator.

14.3.8 Add 2.0 grams of conditioned sodium sulfate to a 15ml amber vial with a Teflon cap. Transfer sample from the 10 ml volumetric flask to the 15ml vial.

14.3.9 Record all lot numbers, prepping analyst, times and dates on prep bench sheet (see FSV4-02).

14.3.10 Shake sample for two minutes.

14.3.11 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extracts through the glass wool and collect 5ml of the extract in a tube or vial.

14.3.12 No concentration step is need for this extraction. Sample can potentially require cleanup prior to analysis. Refer to attachments I and II or the GPC SOP (Rev. 0) for sample cleanup options.

14.4 Sample Concentration Methods 3510 and 3546

14.4.1 Place glass microfiber filter paper into a glass funnel. Fill the filter paper two-thirds with sodium sulfate. Rinse filter paper, sodium sulfate, funnel, and TurboVap tube with methylene chloride. (Kuderna-Danish (K-D) apparatus can be employed at this step)

14.4.2 Quantitatively pour the extract through the filter and funnel seated on a 200mL TurboVap concentrator tube (Kuderna-Danish (K-D) apparatus can be employed at this step). For microwave extraction, shake the tube for 30 seconds then pour both the extraction solution and the sample matrix from the microwave tube into the funnel and filter paper seated on the TurboVap apparatus, being careful to not allow the extract to splash out of the funnel as the sample matrix pours into it. Rinse the beaker, VOA vial or microwave tube three times with methylene chloride. Add these rinses through the filter and funnel into the concentrator tube.

14.4.3 Before placing the concentrator tube into the unit, make sure that the water is at the appropriate level and temperature. Place the concentrator tube into the TurboVap unit and then lower gently so the tubes rest firmly on the sensor tray. The proper nitrogen pressure condition is set between 6-8 and the temperature 45ºC. It is critical that the analyst watch the extract as it concentrates. THE EXTRACT CANNOT GO TO DRYNESS.

14.4.4 When the extract volume reaches approximately 4-6 mL, remove the concentrator tube from the bath and add 40 mLs of hexane. Use a pipet to aid in mixing of the solvents by drawing up the extract and expelling solvent, then gently stir the solvent to ensure that the methylene chloride and hexane are well mixed. Place the concentrator tube back into the unit. Concentrate the extract to approximately 5 mL. Remove the concentrator tube from the bath and allow the concentrator tube to cool completely.

14.4.5 With a disposable Pasteur pipet draw up the extract and rinse the sides of the concentrator tube. Repeat this rinsing several times. (Note: If the sample extract appears highly colored or has a strong petroleum type odor, a sulfuric acid clean-up will be required.) Transfer the extract from the concentrator tube using a Pasteur pipet to a 10mL TC volumetric flask. Rinse the concentrator tube with approximately 3mLs of hexane. Transfer the rinse to the volumetric flask. Bring sample up to a 10 mL volume with hexane. Transfer sample into a labeled 12mL amber vial. Highly contaminated samples may not adequately concentrate down to 10ml. Such samples shall be transferred to an appropriate volume volumetric flask and brought to volume with hexane. Record the final extract on the injection extraction bench sheet.

14.4.6 Record all lot numbers, prepping analyst, times and dates on prep bench sheet (see FSV4-02).

14.4.7 The sample extract is now ready for analysis. If samples are not analyzed immediately store the sample extract in a refrigerator (0-6 C).

14.4.8 Samples can potentially require cleanup prior to analysis. Refer to attachments I and II or the GPC SOP (Rev. 0) for sample cleanup options.

15.0 Data Analysis and Calculations

15.1 Before initial calibration or sample analysis, a priming standard will be injected at a suggested level 2x the highest linearity point. A clean hexane blank must be analyzed to determine baseline characteristics. If the instrument has been in use within 24 hours prior to analysis, this step can be omitted.

15.2 Verify calibration each twelve hour shift by injecting a Continuing Calibration Verification standard (CCV), containing Aroclors 1016/1260, prior to conducting any sample analysis. A CCV must be injected at the beginning of the sequence, and at intervals of no less than one per 20 samples injections or twelve hours (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded), and at the end of each sequence. The variance of any given Aroclor 1016/1260 shall not be more than +/- 20% difference. If a different Aroclor is chosen for the continuing calibration verification, that CCV is subjected to the same QC criteria as the original CCV of Aroclors 1016/1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst can include a standard for one or all of these Aroclors after the 1016/1260 CCV for pattern reference.

15.3 Before the initial sample batch analysis, inject the sample prep batch method blank to demonstrate that the instrument, as well as the extraction procedure, is free from contamination. All compounds must be below the method detection limit.

15.3.1 Samples can be directly injected after the successful analyses of the calibration curve, ICV, CCV and method blank. There can be up to 20 samples in an analytical batch. A matrix spike/matrix spike duplicate and laboratory control spike must be analyzed with every analytical batch. Recoveries will be within laboratory generated QC limits or client specified limits for all surrogate, matrix spike/matrix spike duplicate and laboratory control spike injections.

15.3.2 All positive detects in the associated sample must be confirmed by a second column. Positive detects are identified and quantitated using both detectors. The results between primary and secondary columns must be within +/- 40 % difference, (if greater than 40% the target analyte is qualified with a "P"). If there is no evidence of chromatographic problems, then it is appropriate to report the lower result (method 8000C). Specific projects or programs will require that the higher of the two columns results be reported.

15.3.2.1 QSM: Report from the primary column unless overlapping peaks are causing erroneously high results, then report the non-affected result. Qualify the data with a "Q" flag if target analyte is not confirmed by second column confirmation.

15.3.3 Each sample analysis must be bracketed with passing continuing calibration verification standards. If the CCV standard fails to meet QC criteria, all samples that were injected after the last standard which met QC criteria must be re-analyzed.

15.3.4 The data acquisition software generates a ug/ml concentrations which can then be applied to the final calculation to give sample concentrations. Samples with results exceeding calibration range are diluted accordingly in hexane and re-analyzed.

15.4 Using the slope (m) and the intercept (b) from this equation, the concentration of the sample (ug/ml) is calculated and appears on the report page following the chromatogram.

Water samples:

$$C_S = [(C_C)(V_E)(D)]/V_S$$

Soil samples:

$$C_S = [(C_c)(V_E)(D)]/[(W)(S)]$$

Wipe samples:

$$C = [(C_c)(V_E)(D)]$$

Where: C_S = Concentration of sample in ug/L for waters and mg/kg on a dry weight basis for soils

C_c = Concentration from the curve (ug/ml)

C = Concentration in total ug

V_E = Total volume of sample extract (after concentration) in ml

V_S= Volume of water sample in liters

D = Dilution factor if extract was diluted

W = Weight of wet soil sample in grams

S = Total percent solids, expressed as: percent total solids/100

16.0 Method Performance

See QAM Appendix 9.

17.0 Pollution Prevention

See QAM Appendix 9.

18.0 Data Assessment & Acceptance Criteria for QC Measures

18.1 If the initial analysis of a sample or a dilution of the sample has a concentration of a particular PCB that exceeds the calibration range, the sample must be re-analyzed at a dilution. If the initial sample exhibits interference such as sulfur, petroleum hydrocarbons, or other baseline interference, the sample must under go sample clean-up. Refer to Attachments I and II or the GPC SOP (Rev. 0) for sample clean-up procedures. The method blank and laboratory control sample must accompany the sample during the clean-up procedure.

18.1.1 Samples suspected of containing high levels of contamination or samples with known historical data may need to be diluted prior to analysis. Multiple dilutions may be needed to cover the entire working range of the current calibration.

18.2 The qualitative identification of PCBs as Aroclors determined by this method is based on retention time and pattern recognition. This method employs a dual ECD detector with two dissimilar columns. There is a potential for many non-target compounds present in samples to interfere with this analysis, therefore sample extracts can undergo cleanup procedures. The retention times are updated at the midpoint of each new calibration and they are continually updated with the daily continuing calibration verification standards (CCVs). A new method ID is provided for each new sequence with updated retention times or alteration to the operating initial calibration method. If an alteration occurs (other than daily retention time updates), project management and the QA officer will be notified. A description of the alteration will be addressed in the client notes or case narrative.

18.3 Reporting Quantitative Analysis:

18.3.1 When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. Once the standard retention times are compared and the sample retention times have been made, the sample data can be reported. Assessments of all spiked, calibration control samples and standards will also be scrutinized before reporting the data.

18.3.2 When the analyst has finished processing the analytical batch, the results are electronically transferred to the LIMS system where weight to volume corrections, dilution factors, and percent solids adjustments are made. Once the final results have been verified, a checklist (FSV4-01.) is filled out and signed confirming that all the data has been thoroughly scrutinized. At this point, the data is turned over to another qualified analyst for final validation. The second

analyst confirms the results, electronically marks them validated, and signs his or her portion of the checklist (the checklist is included in this SOP). Finally, the validated results are made available to the client services personnel in order for the data to be given to the client or appropriate agencies.

18.3.3 An electronic copy of the data is then filed and archived. The package includes; the sequence run log, checklist, a copy of the bench sheet, the LIMS run log, LIMS prep sheet, verification of calibration data, each sample's chromatogram. All the data is initialed and dated by the analyst. Each sequence file header is labeled with the date of sequence.

19.0 Corrective Measures for Out-of-Control Data

See QAM Appendix 9.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

See QAM Appendix 9.

21.0 Waste Management

See QAM Appendix 9.

22.0 Equipment / Instrument Maintenance, Computer Hardware & Software & Troubleshooting

See QAM Appendix 9.

23.0 References

23.1 USEPA, SW-846, 3rd Ed. Chapters 2&4, Method 8000C. March 2003.

23.2 USEPA, SW-846, "Polychlorinated Biphenyls(PCBs) by Gas Chromatography", Method 8082A Revision 0. December 1996.

23.3 USEPA, SW-846, "Organic Extraction and Sample Preparation", Method 3500B Revision 2. December 1996.

23.4 USEPA, SW-846, "Separatory Funnel Liquid-Liquid Extraction", Method 3510C Revision 3. December 1996.

23.5 USEPA, SW-846 "Microwave Extraction", Method 3546 Revision 0. February 2007.

23.6 USEPA, SW-846 "Gel-Permeation Cleanup" Method 3640A Revision 1. September 1994.

23.7 USEPA, SW-846 "Sulfur Cleanup", Method 3660B Revision 2, December 1996.

23.8 USEPA, SW-846 "Florisil Cleanup", Method 3620 Revision 3, February 2007.

23.9 USEPA, SW-846 "Solid Phase Extraction" Method 3535A Revision 1, February 2007.

23.10 USEPA, SW-846 "Waste Dilution" Method 3580A Revision 1, July 1992.

23.11 CT Laboratories Quality Manual, most recent version

23.12 Department of Defense, *Quality Systems Manual for Environmental Laboratories*, Version 5.0, DoD QSM, March 2013 or most recent revision

23.13 National Environmental Laboratory Accreditation Conference (NELAC), 2003 *NELAC Standard Chapters 1 to 6*, EPA/600/R-04/003, June 5, 2003 or most recent version

23.14 ISO. 2005. *General requirements for the competence of testing and calibration laboratories*. ISO.IEC 17025:2005

ATTACHMENT I
SULFUR CLEANUP
METHOD 3660

1.0 Identification of Test Method

This method is designed to follow the procedures and QC requirements found in EPA SW-846 method 3660.

2.0 Applicable matrix or matrices

Semi-Volatile organic compounds are quantitated from a variety of matrices. This method is applicable to nearly all types of samples regardless of water content, including ground water, surface water, wastewater, soils and sediments, as well as other matrices noted in SW-846 method 8081B, 8082A.

3.0 Detection Limits

NA

4.0 Scope & Application, including components to be analyzed

This method is used to clean up Semi-Volatile Organochlorine Pesticides and Polychlorinated Biphenyls in many types of solid waste matrices, soils, and groundwater. See Tables 1.0 for typical target analyte list (TAL) in SOP 8081 and 8082.

5.0 Method Summary

This method covers the procedures used to eliminate sulfur interference from pesticide extracts. Elemental sulfur is indicated by the presence of white crystals in the sample extract, or, upon analysis, a broadband interference from the solvent front.

6.0 Definitions

NA

7.0 Interferences

7.1 Solvents, reagents, glassware, and other sample processing hardware can yield artifacts and /or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Refer to each method for specific guidance on quality control procedures.

7.2 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

7.3 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, can cause degradation of certain analytes.

8.0 Safety

8.1 Gloves and protective clothing shall be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure must utilize appropriate laboratory safety systems.

8.2 The toxicity and carcinogenicity of the chemicals used in this method are not precisely defined. Each chemical and sample shall be treated as a potential health hazard, so care must be taken to prevent undue or extensive exposure.

9.0 Equipment & Supplies

9.1 Mechanical shaker or mixer

9.2 Pasteur Pipettes; 5 ¾" and 9" (VWR #14672-200 and -300) or equivalent.

9.3 Disposable culture tubes – 25 mL with Teflon-lined screw caps.
(vials - Fischer 1496226F, Caps - Fisher 1495936A) or equivalent

9.4 Volumetric flask (Class A TC) 100 mL.

10.0 Reagents & Materials

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 shall 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 De-ionized water (Milli-Q processed), analyte free or equivalent.

10.3 Acetone, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date.

10.4 Hexane, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date.

10.5 2-Propanol, pesticide grade. Used within one year of opening or before the manufacturers expiration date.

10.6 Tetrabutylammonium (TBA) sulfite reagent (Aldrich Part # 86847-1EA-F or equivalent). Used within five years of opening or before the manufacturers expiration date.

10.7 Tetrabutylammonium hydrogen sulfate (Aldrich Part # 155837-25G or equivalent). Used within five years of opening or before the manufacturers expiration date.

10.8 Sodium sulfite, (Aldrich Part# 239321-500G or equivalent). Used within five years of opening or before the manufacturers expiration date.

10.9 Nitric Acid, HNO_3, 1:1(v/v). Used within six months of mixing or before the manufacturers expiration date.

10.10 Copper powder, (UCT Part# ECCU01K or equivalent).

10.11 Tetrabutylammonium (TBA) – sulfite reagent (ACROS 42010-5000 or equivalent). Used within five years of opening or before the manufacturers expiration date.

10.12 Sodium sulfate (granular, anhydrous 60/120 mesh, JT Baker # 3375-05) or equivalent. If sodium sulfate passes in house lot check, it can be used as is and stored in air tight glass jar. Otherwise condition sodium sulfate by heating to 400°C for 4 hours in a shallow glass tray loosely covered with foil and recheck for purity. Sodium sulfate will be stored in airtight glass jars and used within five years of opening or before the manufacturer's expiration date.

11.0 Sample Collection, Preservation & Storage

NA

12.0 Quality Control

This SOP is designed to follow a variety of different projects and programs requirements. Table 3 in SOP's 8081B and 8082A are designed to illustrate the control steps and provisions required to adequately producing acceptable data.

13.0 Calibration & Standardization

NA

14.0 Procedure

14.1 TBA Solution

14.1.1 Prepare reagent by dissolving 3.39g tetrabutylammoniuhydrogen sulfatete in 100ml organic-free water. To remove impurities, extract this solution three times with 20ml portions of hexane. Discard the hexane extracts. Add 25g 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 can be stored at room temperature for at least one month.

14.1.2 Pipet 1.0 mL of pesticide extract into a 25 mL culture tube.

14.1.3 Add 1.0 mL TBA – sulfite reagent and 2 mL iso-propanol to the tube and cap.

14.1.4 Shake for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if crystals are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

14.1.5 Add 5 mL distilled water and shake for at least 5 minutes. Allow the sample to stand for 5-10 minutes. Transfer the hexane layer to injection vials and/or storage vials.

14.1.6 Analyze the extracts by gas chromatography.

14.1.7 Verify that the TBA-sulfite is free from contamination by shaking out 1.0 mL of TBA – sulfite with 10 mL of hexane and analyze.

14.1.8 Process all quality control samples (e.g., spikes, blanks and duplicates) along with any samples.

14.1.9 Verify that recoveries of pesticides are greater that 80% by processing a standard (CCV) through the procedure.

14.2 Copper Powder

14.2.1 Remove oxides by treating the copper powder with dilute nitric acid, rinse with organic free reagent water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen.

14.2.2 Concentrate the sample to exactly 1.0ml or other known volume. Perform concentration using the techniques described in the appropriate 3500 series method.

14.2.3 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the concentration tube. Transfer 1.0ml of the extract to the calibrated centrifuge tube.

14.2.4 Add approximately 2g of cleaned copper powder to the centrifuge tube. Vigorously mix the extract and the copper powder for at least 1 minute on the mechanical shaker. Allow phases to separate.

14.2.5 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1 ml of extract. This step is necessary to prevent further degradation of the pesticides.

15.0 Data Analysis & Calculations

NA

16.0 Method Performance

NA

17.0 Pollution Prevention

See QAM Appendix 9.

18.0 Data Assessment & Acceptance Criteria for QC Measures

NA

19.0 Corrective Measures for Out-of-Control Data

NA

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

NA

21.0 Waste Management

See QAM Appendix 9.

22.0 Equipment / Instrument Maintenance, Computer Hardware & Software & Troubleshooting

NA

23.0 References

USEPA, SW-846, 3rd Ed. Method 3660. December, 1996.

ATTACHMENT II
FLORISIL CARTRIDGE CLEANUP
METHOD 3620

1.0 Identification of the test method

This method is designed to follow the procedures and QC requirements found in EPA SW-846 method 3620.

2.0 Applicable matrix or matrices

This method is applicable to nearly all types of samples regardless of water content, including ground water, surface water, wastewater, soils and sediments, as well as other matrices noted in SW-846 method 8081B, 8082A.

3.0 Detection Limits

NA

4.0 Scope & Application, including components to be analyzed

This method is used to clean up Semi-Volatile Organochlorine Pesticides and Polychlorinated Biphenyls in many types of solid waste matrices, soils, and groundwater. See Tables 1.0 for typical target analyte list (TAL) in SOP 8081 and 8082.

5.0 Method Summary

5.1 This method describes procedures for Florisil cleanup of solvent extracts of environmental samples using solid-phase extraction cartridges. The cartridge cleanup protocol uses solid-phase extraction cartridges containing 40 µm particles of Florisil (60 D pores). Each cartridge is rinsed with solvent immediately before use. The sample extract is loaded onto the cartridge which is then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The eluate will be further concentrated prior to gas chromatographic analysis.

5.2 Florisil has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes. Additionally, Florisil is considered good for separations of steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates. Florisil cleanup can be accomplished using glass chromatographic column packed with Florisil or using solid-phase extraction cartridges containing Florisil. This method includes procedures for cleanup of sample extracts containing the following analyte groups:

Chlorinated hydrocarbons
Organochlorine pesticides
Organophosphates
Organophosphorus pesticides
PCBs
Phthalate esters
Nitrosamines
Nitroaromatics

Haloethers
Aniline and aniline derivatives

6.0 Definitions

Florisil: a registered trade name of U. S. Silica Co., is a magnesium silicate with basic properties. It is used to separate analytes from interfering compounds prior to sample analysis by a chromatographic method.

7.0 Interferences

7.1 A reagent blank will be prepared and analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples. The procedures for reagent purification outlined here will be considered to be the minimum requirements for use of this method. More extensive procedures shall be necessary to achieve lower levels of interferences for some analytes. During the evaluation of the cartridge clean-up procedure, phthalate esters were detected in the Florisil cartridge method blanks at concentrations up to 400 ng per cartridge. Therefore, complete removal of the phthalates esters from Florisil cartridges will not be possible.

7.2 Solvents, reagents, glassware, and other sample processing hardware can yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Refer to each method for specific guidance on quality control procedures.

7.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

7.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, can cause degradation of certain analytes.

8.0 Safety

8.1 Gloves and protective clothing shall be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure must utilize appropriate laboratory safety systems.

8.2 The toxicity and carcinogenicity of the chemicals used in this method are not precisely defined. Each chemical and sample shall be treated as a potential health hazard, so care must be taken to prevent undue or extensive exposure.

9.0 Equipment & Supplies

9.1 Vacum manifold - VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack, funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing. The manifold is required for use of the cartridge cleanup protocol.

9.2 Organomation Nitrogen blow down concentrator (N-Evap).

9.3 Pasteur Pipettes; 5 ¾" and 9" (VWR #14672-200 and -300) or equivalent.

9.4 Concentrator tube, 10.0 mL, graduated (Fisher # K570051-1025 or equivalent).

10.0 Reagents & Materials

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 shall 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 Acetone, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date.

10.3 Hexane, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date.

10.4 Methylene chloride, pesticide grade, analyte free. Used within one year of opening or before the manufacturers expiration date. Or stored in large carboy tank provided by manufacturer and used within one year of opening or before the manufacturer's expiration date.

10.5 Florisil extraction cartridges, 1000MG/6ML (UCT EUFLSA1M6) or equivalent.

10.6 Florisil cartridge pesticide check solution - Prepare a solution containing the following analytes in hexane:

BHCs
Heptachlor
BHC
Endosulfan I
Dieldrin
Endrin
4,4'-DDD
4,4'-DDT
Methoxychlor
Tetrachloro-m-xylene
Decachlorobiphenyl

11.0 Sample Collection, Preservation & Storage

NA

12.0 Quality Control

12.1 This SOP is designed to follow a variety of different projects and programs requirements. Table 3 in SOP's 8081B and 8082A are designed to illustrate the control steps and provisions required to adequately producing acceptable data.

12.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. A recovery check must be performed using standards of the target analytes at known concentrations. The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered are be used to process the samples. A check shall also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

12.3 Organochlorine pesticides - To check each new lot of Florisil cartridges before use, perform the following in duplicate. Combine 0.5 mL of the 2,4,5-trichlorophenol solution, 1.0 mL of the pesticide solution, and 0.5 mL of hexane in a vial. Condition the cartridge and then perform the cartridge cleanup Elute the cartridge with 9 mL of acetone/hexane (10/90, v/v) only. Reduce the volume to 1.0 mL and analyze. The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110 %, if the recovery of trichlorophenol is less than 5 %, and if no peaks interfering with the target analytes are detected.

13.0 Calibration & Standardization

NA

14.0 Procedure

14.1 Whenever Florisil is used to fractionate groups of target compounds (rather than to simply remove potential interference) it is critical that the specific fractionation scheme be validated using spiked solutions or spiked sample extracts that contain most or all of the analytes of interest. This is particularly important when the Florisil cartridge techniques are employed, as the differences between the various cartridge formats and manufacturers can affect the fractionation patterns. In addition, it will be useful to archive any fractions not originally intended for analysis in the event that the fractionation scheme chosen does not yield the intended results. Once the determinative analysis has been performed and demonstrates that the fractionation has been successful, such archived fractions can be disposed of in an appropriate manner. However, if the fractionation did not perform as intended, the analytes of interest contained in the archived fractions will be able to be analyzed or combined with the other fraction(s) for reanalysis.

14.2 Following Florisil cleanup, extracts will require further concentration and/or solvent exchange.

14.3 Cartridge Evaluation

14.3.1 The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered are be used to process the samples. A check shall also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

14.3.2 To check each new lot of Florisil cartridges before use, perform the following in duplicate.

14.3.3 Combine 0.5 ml of 2,4,5-Trichlorophenol solution in Section 5.5 and 0.5 ml of pesticide spiking solution in Section 5.6 in a 2ml autosampler vial.

14.3.4 Arrange the cartridges on the manifold in the closed-valve position.

14.3.5 Turn on the vacuum pump and set the vacuum to 10 in (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates can be controlled by opening and closing cartridge valves.

14.3.6 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

14.3.7 Slowly open cartridge valves to allow the hexane to pass through the cartridges.

14.3.8 Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed.

14.3.9 Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

14.3.10 Add the spiking solution in 6.2.3 to the Florisil cartridge.

14.3.11 Elute the cartridge with 9 ml of acetone/hexane (10/90, v/v). Collect the extraction in a 15 ml test tube.

14.3.12 Transfer extract to a concentrating thimble. Using the nitrogen blow down apparatus, concentration the extract down to 1ml and analyze by Method 8081A.

14.3.13 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110%, if the trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected.

14.4 Handling sample extracts

14.4.1 Most sample extracts will have to be concentrated to a smaller volume prior to the use of Florisil cleanup. The extract volume is a function of the analytical sensitivity necessary to meet the project objectives. The extract volume will also affect the ability of the Florisil to separate target analytes from potential interferences. Applying large extract volumes to the cartridges will cause poor results. Consult the appropriate extraction and determinative methods for the details on final extract volumes, extract concentration techniques, and solvent exchange procedures.

14.4.2 Reduce the sample extract volume to 10.0 mL prior to cleanup. The extract solvent will be hexane for these analytes. In most cases, given the sensitivity of the determinative methods, only 1 mL of the 10.0 mL extract needs to be subjected to the Florisil cleanup procedure. The remaining 9 mL will be archived for later use, if needed.

14.4.3 Place Florisil cartridges on manifold. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Condition the cartridges by adding 4 ml of hexane. Slowly open the cartridge valve and collect the eluate into the collection vial. Allow a few drops of hexane to pass through the cartridge to remove any air bubbles. Close valve and allow solvent to soak the entire sorbent bed for five minutes. Do not turn off vacuum.

14.4.4 Slowly, open the valve to allow the hexane to pass through the cartridge. Close valve when about 1 mm of hexane is remaining above the sorbent bed.

14.4.5 Add 1.0 ml of extract to the Florisil cartridge. Allow the extract to pass through the cartridge at a rate about 2 ml per minute.

14.4.6 Before extract goes below the surface of the sorbent bed, add 9 ml of hexane/acetone (90/10, v/v) to the cartridge.

14.4.7 After extract has been collected, concentrate sample down to 1.0 ml. Refer to Section 9.5 for concentration techniques.

14.4.8 The following procedures are used to separate the organochlorine pesticides from PCBs:

14.4.8.1 Add 3 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 1 and it will contain the PCBs and a few of the organochlorine pesticides.

14.4.8.2 Close the cartridge valve, replace the collection vial, and add 5 mL of methylene chloride/hexane (26/74, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2 and it will contain most of the pesticides.

14.4.8.3 Close the cartridge valve, replace collection vials, and add 5 mL of acetone/hexane (10/90, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 3 and it will contain the remaining pesticides.

14.4.8.4 As needed, perform a solvent exchange and adjust the final volume of the eluant to 1 ml.

15.0 Data Analysis & Calculations

NA

16.0 Method Performance

NA

17.0 Pollution Prevention

See QAM Appendix 9.

18.0 Data Assessment & Acceptance Criteria for QC Measures

NA

19.0 Corrective Measures for Out-of-Control Data

NA

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

NA

21.0 Waste Management

See QAM Appendix 9.

22.0 Equipment / Instrument Maintenance, Computer Hardware & Software & Troubleshooting

NA

23.0 References

USEPA, SW-846, 3rd Ed. Method 3620. December, 1996.

CT Laboratories Quality Manual, current revision.
Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.0, July 2013 or most recent revision.

National Environmental Laboratory Accreditation Conference (NELAC), 2003 NELAC Standard Chapters 1 to 6, EPA/600/R-04/003, June 5, 2003 or most recent version.

ISO. 2005. General requirements for the competence of testing and calibration laboratories. ISO17025.

Table 3.0
Summary of Method Quality Objectives for Method 8082- PCBs by aroclors

Quality Control Element	Frequency of Implementation	Acceptance Criteria	Corrective Action
Initial Calibration Aroclors 1016/1260 or client specified aroclor(s)	Initial Calibration prior to sample analysis.	1. RSD for each analyte $\leq$ 20% 2. Linear – least squares regression r $\geq$ 0.995. 3. Non-linear regression $r^2 \geq 0.99$. (6 points shall be used for second order)	For aroclor analysis, a mixture of aroclors 1016/1260 is normally used to establish detector calibration linearity, unless project specific arolclor(s) is required. Linearity must fit one of acceptance criteria. Correct the problem and repeat ICAL. Single level CFs for the remaining arolcors must be established with each initial calibration.
Initial Calibration Verification (ICV)	Immediately following the ICAL	Difference $\leq$20% From a second source (different lot or manufacturer)	If ICV falls outside QC criteria, reanalysis must take place. If ICV still fails, it will be necessary to correct to problem, or it will be appropriate to repeat the initial calibration curve or to qualify the analyte with "Z". QSM: No samples will be analyzed until the problem has been corrected.
Continuing Calibration Verification (CCV)	Every twelve hours or every twenty samples (which one comes first) QSM: Every ten samples, Prior to sample analysis, after every 10 field samples, and at the end of the analysis sequence.	Difference $\leq$20%	If CCV falls outside QC criteria, reanalysis must take place. If CCV still fails, it will be necessary to correct to problem, or it will be appropriate to repeat the initial calibration curve or to qualify the analyte with "Z". Exception to the above, if the acceptance limits are exceeded high and the analyte is not detected in the sample the verification standard has passed (analyte would have been detected if present). QSM: No samples will be analyzed until the problem has been corrected. Flagging is only appropriate in cases where the sample cannot be reanalyzed.
Retention Time Window (RTW)	Retention Times will be set using the midpoint standard in the ICAL or the RT in the CCV run at the beginning of each analytical shift.	Shift less than ± 3 times the absolute Standard Deviation from the 72 hour RTW study, with a minimum width of 0.03 minutes	

Table 3.0
Summary of Method Quality Objectives for Method 8082- PCBs by aroclors

Quality Control Element	Frequency of Implementation	Acceptance Criteria	Corrective Action
MRL Level Verification Check standard at Reporting Limit. (LCG only)	Beginning and End of 12 hr. sequence or program specified.	70-130% or project specific/client limits	Note failures in case narrative. If MDL check was run at the end and acceptable do not reject data.
Method Blank (MB)	1 per sample batch ≤ 20 samples of the same matrix	Analytes must not he higher than the highest of the following: 1/2 MRL, or 5% of the regulatory limit, or 5% of the associated sample concentration. QSM = ½ MRL	If sample is available and within holding times, sample associated with method blank needs to be reprepped. If no sample is available, qualify the data with a "B" to all associated positives when less than 5X blank concentration. QSM: Apply "B" to all results for the specific analytes in all samples in the associated preparatory batch.
Laboratory Control Sample (LCS)	1 per sample batch ≤ 20 samples of the same matrix	1.0 Client specified limits 2.0 QSM – use LCS criteria 3.0 In-house limits	If LCS fails percent recoveries, correct problem and re-analyze the LCS. If LCS recoveries are still outside QC control limits, and if there is sample remaining, the sample batch must be reprepped. If there is not sample available for reanalysis, qualify the failing analytes with a "Q".
Matrix Spike (MS)	1 per sample batch ≤ 20 samples of the same matrix	1.0 Client specified limits 2.0 QSM – use LCS criteria 3.0 In-house limits	No action is taken based on MS recovery alone, use of professional judgement. For recoveries outside QC criteria, qualify out lying analyte(s) in the parent sample with "M".
Matrix Spike Duplicate (MSD)		1.0 Client specified limits 2.0 QSM RPD < 30% 3.0 In-house limits	No action is taken based on MSD results alone, use of professional judgement. If RPD is outside QC criteria, then qualify the out lying analyte(s) in the parent sample with "Y".

Table 3.0
Summary of Method Quality Objectives for Method 8082- PCBs by aroclors

Quality Control Element	Frequency of Implementation	Acceptance Criteria	Corrective Action

Surrogates	Every sample and QC	1.0 Client specified limits 2.0 QSM – use LCS criteria 3.0 In-house limits	Rerun sample. If no apparent matrix interference noticed re-extract sample. If no sample is available, qualify the surrogate with "S". QSM: For QC and field samples; correct problem, reprep, and re-analyze all failed samples or failed surrogates in the associated batch, if sufficient sample material is available.
Target Analyte Confirmation	Whenever a positive is detected, check agreement between primary and secondary columns.	RPD $\leq$ 40% QSM: Discuss in case narrative about qualified data.	Report from primary column unless it can be scientifically excluded **If present and RPD >40%** Flag with "P" qualifier and discuss in case narrative if appropriate..

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Analytical Run # 8082 PCB Analysis Data Review Checklist (Example)

Sequence Date	*Analyst / Data Interpreter*	*Independent Reviewer*	*Date of Review*	*Approved*
				Yes or No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. INITIAL CALIBRATION (ICAL)						
a. Was the PCB initial calibration (Aroclor 1016/1260) performed using a minimum of five varying standard concentration levels on two dissimilar columns?	Lowest standard at or near MRL					
b. Is the variation between calibration response factors for all concentration levels <20% RSD, is r^2 >.990, or r > 0.995 for the regression line?	RSD <20%, r^2 >.990, r>0.995					
c. Was each ICAL uniquely identified (i.e. Standard Number)?						
d. Were there Calibration Factors (CF) established for the remaining Aroclors?						
d. Was an initial calibration blank (ICB) analyzed?						
2. INITIAL CALIBRATION VERIFICATION (ICV)						
a. Were there second source ICVs for all Aroclors analyzed after the initial calibration and prior to analysis of any samples?	Second source					
b. Were the recoveries for the ICVs within program limits?	%Recovery					
c. Was the ICVs uniquely identified (i.e. Standard Number)?						
3. CONTINUING CALIBRATION VERIFICATION (CCV)						
a. Were CCVs (Aroclor 1016/1260) analyzed at the beginning of the sequence, after every 12 hours or every 20 samples (which ever comes first) and at the end of the analytical run? QSM = every ten sample injections.						
b. Were the recoveries for the CCVs within program limits?	%Recovery					
c. Were confirmed Aroclor detects processed using the appropriate Aroclor method?						
d. Was each CCV uniquely identified (i.e. Standard Number)?						

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8082 PCB Analysis Data Review Checklist Continued

Requirement:	Acceptance	Analyst Review	Independent Review	Comments:

	Criteria	Yes	No	Yes	No	(indicate reference to an attachment if necessary)
4. BLANKS						
a. Was the method blank (MB) analyzed prior to the analysis of samples?						
b. Was the MB result less than ½ the reporting limit (RL) or 5% of the sample amount?						
c. Was a MB prepped and analyzed at a frequency of one per Prep Batch?	Batch < 20 samples					
5. LABORATORY CONTROL SAMPLE (LCS)						
a. Was a LCS analyzed at a frequency one per Prep Batch?	Batch < 20 samples					
b. Were the LCS recoveries in each LCS within the acceptance criteria?	In-house limits or client specified limits					
6. MATRIX SPIKES						
a. Was a matrix spiked (MS) sample analyzed at a frequency one per Prep Batch?	Batch < 20 samples					
b. Were MS recoveries in each MS within the acceptance criteria?	In-house limits or client specified limits					
7. MATRIX SPIKE DUPLICATE						
a. Was a duplicate matrix spike sample analyzed at a frequency one per Prep Batch?	Batch < 20 samples					
b. Were MSD recoveries within the acceptance criteria?	In-house limits or client specified limits					
c. Is the relative percent difference (RPD) between a matrix spike (MS) and its' duplicate (MSD) within the acceptance criteria?	In-house limits or client specified limits					

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8082 PCB Analysis Data Review Checklist Continued

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
8. SAMPLES (INCLUDING BLANKS, STANDARDS, AND QC SAMPLES)						

a. Are chromatogram characteristics, including peak shapes and areas, consistent with those of the CCV?						
b. Are surrogate recoveries for all samples, blanks, standards, and QC samples within acceptance criteria?						
c. Were all samples having analytes detected in amounts exceeding the calibration range diluted and reanalyzed?						
d. Were all samples extracted within holding times and analyzed within 40 days of extracting?	Analysis within 40 days of extraction					
e. Did the samples require additional cleanup steps? (i.e. acid treatment, florisil, and sulfur treatment)	Acid, Florisil, GPC, Sulfur Treatments					
f. Was there a hexane injection performed prior to sample analysis?						
g. Was there a priming standard injected prior to sample analysis?						
9. RECORDS AND REPORTING						
a. Is the Analytical Run, Prep Batch and Extraction sheets, Summary sheets, Sequence file, analytical data, and method transfer to PDF format?						
b. Are reported results whose amounts exceeded the acceptance criteria flagged with an appropriate qualifier in LIMS and, if needed, a NCR completed?						
c. Do all values, dilution factors and qualifiers listed on the raw reports match the LIMS data?						
d. Is the ICAL method referenced on the Raw Data?						

FSV4-02 PCB Extraction Bench Sheet (Example)

Pesticides/PCB Extraction Bench Sheet

(SOP Reference #'s 8081 & 8082)

3510=WATER
3545=PFE or 3546=Microwave >>
(PFE=Pressurized Fluid Extraction)

Prep Batch #:	
Prep Method:	
Analyst:	
Date:	
Start Time:	
End Time:	

Analysis Methods
8081 = Pesticides
8082 = PCBs

Matrix: _____

Balance: _____

Concentration By: _____

Concentration Date: _____

Reagent:	Lot #
NA_2SO_4	
Diatomaceous Earth	
Dionex Solution	
$MeCl_2$	
Acetone	
Hexane	

Microwave Cell #	Sample ID		(Solids) Sample Weight (g)	(Liquids) Sample Volume (L)	Final Volume (ml)
		(MB			10
		(LCS)			10
					10
		Comments:			10
					10
					10
					10
					10
					10
					10
					10
					10
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					10
					10
					10
					10
					10
					10
					10
					10
					10
		(MS) Parent Sample			10
		(MSD)			10

MB=Method Blank, LCS=Laboratory Control Sample, MS=Matrix Spike, MSD=Matrix Spike Duplicate, Tox=Toxaphene & Chlor=Technical chlordane

MS/MSD/ LCS Spike Amount (ml): _____
Spike Concentration (ug/mL): _____
Spike Reference #: _____

Surrogate Spike Amount (ml): _____
Surrogate Spike Conc. (ug/mL): _____
Surrogate Spike Reference #: _____

Tox/Chlor Spike Amount (ml): _____
Tox/Chlor Spike Conc. (ug/mL): _____

Tox/Chlor Spike Reference: _____

Relinquished to: _____
Date: _____

Reviewed By: _____
Date: _____

Pest-PCB Prep 3/12/201208:34

Revision Number	Description of Changes	Date

11	Document changed to incorporated administrative requirements of ISO 17025 and QSM 5.0. Descriptions of changes have not been tracked in previous versions of this document.	08/19/2013

CT LABORATORIES

delivering more than data from your environmental analyses

STANDARD OPERATING PROCEDURE

SV 007 Semi-volatile Organic Compounds by GC/MS SIM

Review Date: 05/28/2019

05/29/2019

Technical Review by: Date

05/29/2019

Approved by: QA Officer Date

Table of Contents

1. SCOPE OF APPLICABILITY

1.1. This method is designed to follow procedures and QC requirements found in EPA SW-846 methods 8000 and 8270D in order to determine quantities of semi-volatile organics in a variety of different sample matrices.

1.2. Semi-volatile compounds are quantitated from a variety of matrices. This method is applicable to nearly all types of samples, including: ground water, surface water, wastewater, soils and sediments, and other matrices noted in SW-846 method 8270D.

1.3. Method 8270D is used to determine the amounts of various Polynuclear Aromatic Hydrocarbons (PAHs), pesticides and other selected semi volatile organic compounds in extracts from solid and aqueous matrixes. Gas Chromatography/Mass Spectrometry (GC/MS) is employed with the mass spectrometer operated in selected ion monitoring mode (SIM) in order to achieve lower detection limits. Target compounds determined by this method, along with their associated surrogates and internal standards, are listed in Tables 1 through 4.

2. SUMMARY OF METHOD

2.1. A sample of a known volume or mass is extracted with solvent. Aqueous samples are prepared by separatory funnel extraction (SOP SV022) or solid phase extraction (SPE) (SOP SV024) and solid samples are prepared by microwave extraction (SOP SV021). The resultant extract is chemically dried and concentrated, if necessary (SOP SV023.

2.2. Extracts for 8270 SIM analysis may be subjected to cleanup measures, depending on the nature of the matrix interference and target analytes. The suggested method of cleanup is Gel Permeation Chromatography (GPC) cleanup (SOP SV014) followed by sulfur removal using copper granules (SOP SV026). After cleanup, the extract is analyzed by injecting a known aliquot into a gas chromatograph equipped with a mass spectrometer detector operated in selected ion monitoring (SIM) mode.

2.3. Identification of target analytes is accomplished by comparing their mass spectra with the spectra of certified commercially-prepared stock standards. Quantitation is accomplished by comparing the response of a major quantitation ion relative to an internal standard using a minimum of a five point calibration curve.

2.4. The procedures contained within this method are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results.

3. DEFINITIONS

3.1. DFTPP: Decafluorotriphenylphosphine. This compound is used to verify that the GC/MS is properly tuned and ready for calibration and sample analysis. The DFTPP standard must also contain Pentachlorophenol, Benzidine, and DDT to assess GC column performance and injection port inertness.

3.2. For definitions of many of the terms applicable to this SOP, see the Glossary located in the Quality Assurance Manual (QAM).

3.3. Quality Assurance Manual (QAM): a document describing the organization and general operations of a laboratory.

3.4. For a list of common acronyms and abbreviations, see the Acronyms located in the QAM.

4. HEALTH AND SAFETY

4.1. Safety glasses, gloves, and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems. Follow all items in the in-house Chemical Hygiene Plan and Health and Safety Manual.

4.2. The toxicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

5. INTERFERENCES

5.1. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and /or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

5.2. Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

5.3. Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes.

5.4. Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interference, further cleanup of the sample may be necessary.

5.5. Mass spectrometer sensitivity, column degradation, and contamination can also contribute to background interferences. The presence of semi-volatile hydrocarbons in the sample extracts may require an appropriate post analysis bake-out time to be incorporated in the method.

6. EQUIPMENT AND SUPPLIES

6.1. GC MS system - Hewlett Packard 6890 GC/7683 autosampler/5973 MSD - An analytical system complete with gas chromatograph suitable for split-splitless injection and all required accessories including syringes, analytical column, mass spectrometer detector, auto sampler, electronic pressure control, vacuum pumps, and HP Chemstation data acquisition system. The data acquisition system consists of an IBM compatible PC with an operating system of Windows 7 and Agilent Environmental Chemstation (MSD Chemstation Rev E.02.02.1431).

6.1.1. Carrier Gas: He at 1.6 mL/min, Constant Flow
6.1.2. Injector Temperature: 250º C
6.1.3. Mode: Pulsed Splitless
6.1.4. Inj. Volume: 0.5 µL
6.1.5. Pressure: 13.2 psi
6.1.6. Pulse Pressure: 30.0 psi
6.1.7. Pulse Time: 0.4 min
6.1.8. Purge Flow: 50.0 ml/min
6.1.9. Purge Time: 0.38 min
6.1.10. Total Flow: 53.9 ml/min
6.1.11. Gas Saver On: 20ml/min at 2.0 min
6.1.12. Oven:

6.1.12.1. Initial – 45º (hold for 0.4 min)
6.1.12.2. Ramp – 35º/min
6.1.12.3. Final – 290º
6.1.12.4. Ramp – 4º/min
6.1.12.5. Final – 300º
6.1.12.6. Ramp – 30º/min
6.1.12.7. Final – 325º (hold for 2.0 min)

6.1.13. MS Interface: 300º
6.1.14. MS Source: 280º
6.1.15. SIM Parameters: See Tables 5 through 8

6.2. GC Column: 30m x 0.25 mm ID, 0.25 µm. (J&W DB-5.625 or equivalent).
6.3. Vials - 2.0mL, 12mL, and 60 mL screw cap vials with Teflon lined caps.
6.4. Pasteur Pipets; 5 ¾" and 9"
6.5. Volumetric flask – (Class A) 10, 25, 50, and 100 mL.
6.6. Syringes 10 µL, 100 µL, 500 µL, and 1,000 µL.

7. REAGENTS AND STANDARDS

7.1. Methylene chloride, analyte free, pesticide grade or equivalent.
7.2. Acetone, analyte free, pesticide grade or equivalent.
7.3. Methanol, pesticide grade or equivalent.
7.4. Nitrogen (99.995%purity or greater).
7.5. Helium (99.995%purity or greater).
7.6. Certified Reference Standards:
7.6.1. Semi-volatiles PAH Standard Mix, Absolute Standards #11007 at 2000 µg/mL, or equivalent.
7.6.2. Expanded PAH mix, AccuStandard #Z-014G-FL at 2000 µg/mL, or equivalent.
7.6.3. SIM PAH Surrogate Mix, Phenomenex #AL0-101639 at 2000 µg/mL, or equivalent.
7.6.4. Semi-volatiles Internal Standard Mix, NSI Lab Solutions #C394LP at 2000 µg/mL, or equivalent.
7.6.5. GC/MS Tuning Mix (DFTPP), NSI Lab Solutions #C-491 at 500 µg/mL, or equivalent.
7.6.6. 8270 B/N Surrogate Mix, NSI Lab Solutions #C-376H5 at 5000 µg/mL, or equivalent.
7.6.7. MDA Pest Mix, AccuStandard #MDA-PEST-01-R1 at 500 µg/mL, or equivalent.
7.6.8. EPA Method 507 Pesticide Standard, Absolute Standards #91974 at 100 µg/mL, or equivalent.
7.6.9. Triazine Mix, Absolute Standards #96042 at 100 µg/mL, or equivalent.
7.6.10. Acetochlor, Absolute Standards #71413 at 1000 µg/mL, or equivalent.
7.6.11. 2,3-Dinitrotoluene, SPEX CertiPrep #S-1689 at 1000 µg/mL, or equivalent.
7.6.12. 2,3-Dinitrotoluene, Absolute Standards #71966 at 1000 µg/mL, or equivalent.
7.6.13. 2,4-Dinitrotoluene, Absolute Standards #70160 at 1000 µg/mL, or equivalent.
7.6.14. 2,4-Dinitrotoluene, SPEX CertiPrep #S-1690 at 1000 µg/mL, or equivalent.

7.6.15. 2,5-Dinitrotoluene, AccuStandard #M-8095-SS-03 at 100 µg/mL, or equivalent.
7.6.16. 2,6-Dinitrotoluene, Absolute Standards #70161 at 1000 µg/mL, or equivalent.
7.6.17. 2,6-Dinitrotoluene, SPEX CertiPrep #S-1695 at 1000 µg/mL, or equivalent.
7.6.18. 3,4-Dinitrotoluene, Absolute Standards #71773 at 1000 µg/mL, or equivalent.
7.6.19. 3,4-Dinitrotoluene, AccuStandard #M-8330-IS at 1000 µg/mL, or equivalent.
7.6.20. 3,5-Dinitrotoluene, AccuStandard #M-8330-ADD-39 at 100 µg/mL, or equivalent.
7.6.21. 1,4-Dioxane, Absolute Standards #90871 at 2000 µg/mL, or equivalent.
7.6.22. 1,4-Dioxane, Absolute Standards #70373 at 1000 µg/mL, or equivalent.
7.6.23. 1,4-Dioxane-d8, Absolute Standards #92785 at 10,000 µg/mL, or equivalent.

8. SAMPLE HANDLING AND PRESERVATION

Sample extracts are stored under refrigeration and analyzed within 40 days of extraction.

9. PROCEDURE

9.1. Sample extracts prepared by appropriate extraction, concentration, and cleanup techniques (if necessary) are ready for GC/MS analysis. Refer to the appropriate SOPs for information on sample preparation and cleanup:
9.1.1. Water extraction by separatory funnel SOP SV022
9.1.2. Water extraction by SPE SOP SV024
9.1.3. Soil extraction by microwave SOP SV021
9.1.4. Extract concentration SOP SV023
9.1.5. GPC cleanup SOP SV014
9.1.6. Sulfur cleanup SOP SV026

9.2. Allow the sample extracts to warm to room temperature. Prior to analysis, add 5 µl of internal standard (IS) solution (see Table 10) to 0.5 mL of the concentrated sample extract obtained from sample preparation. Alternatively, 2 µL of (IS) solution is added to 0.2 mL of sample extract in a vial insert.
9.2.1. The internal standards listed in Tables 1 through 4 should permit most compounds of interest to have retention times 0.80-1.20 relative to one of the internal standards.
9.2.2. The base peak ion from the specific internal standard is used as the primary ion for quantitation, unless interferences are noted.

9.3. Before initial calibration or sample analysis, a priming standard can be injected at a level up to twice the highest linearity point.

9.4. Before analysis of any samples or standards (including initial calibration) can begin, the GC/MS system must be hardware tuned so an injection (50 ng or less) of Decafluorotriphenylphosphine (DFTPP) passes the tuning criteria listed in Table 9. See Table 10 for DFTPP solution preparation details.
9.4.1. To acquire the mass spectrum of DFTPP, three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction to eliminate column bleed or instrument background noise is accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP.

9.4.2. The DFTPP standard must also contain Pentachlorophenol, Benzidine, and DDT to assess GC column performance and injection port inertness.
- 9.4.2.1. Degradation of DDT to DDE and DDD must not exceed 20%.
- 9.4.2.2. Benzidine and Pentachlorophenol shall be present at their normal responses and peak tailing evaluated. Benzidine and Pentachlorophenol must each have tailing factors less than 2.
- 9.4.2.3. If the acceptance criteria are not met, instrument maintenance may be necessary.
  - 9.4.2.3.1. Clean the injection port.
  - 9.4.2.3.2. It may also be necessary to trim the capillary column.

9.4.3. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

9.4.4. All subsequent analyses of standards, samples, laboratory quality control (QC) samples, and blanks associated with a DFTPP analysis must use identical MS instrument conditions.

9.5. If initial calibration is to be performed, see section 11 for calibration and standardization information.

9.6. Verify calibration each twelve hour shift by injecting a Continuing Calibration Verification standard (CCV), containing target compounds prior to conducting any sample analysis. A CCV must be injected at the beginning of each twelve hour shift following the DFTPP tune. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid.

9.6.1. It is highly recommended to employ two CCVs at different concentrations to verify the calibration curve when using non-linear calibration. The choice of specific standards and concentrations is generally a method or project specific consideration.

9.6.2. For some programs (i.e. QSM 5.0 and beyond), it is also required to analyze an ending CCV. This should be done at the end of the analytical batch run. The ending CCV percent drift must be less than or equal to 50%.

9.6.3. IS responses and retention times in the CCV standard must be evaluated as soon as is practical after data acquisition. If the retention time for any IS changes by more than 10 seconds from the last calibration check, or if the extracted ion chromatographic profile (EICP) area for any IS changes by a factor of two or more (-50% to 100%) when compared to the CCV level from the initial calibration, then the mass spectrometer must be inspected for malfunctions and corrections must be made. CCVs and associated samples that were analyzed while the system was malfunctioning must be reanalyzed.

9.7. The retention times and standard reference spectra in the method are updated from the CCV for each 12 hour sequence, or from the mid-point of the calibration curve on days when instrument calibration is performed (see section 11 for calibration information). The relative retention time (RRT) of each reported analyte must be within ± 0.06 RRT units of the mean RRT of the calibration standards.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

9.8. Samples can be directly injected after the successful analyses of the initial calibration curve, ICV, DFTPP, and CCV. There can be up to 20 samples per analytical batch plus the associated QC samples. A method blank (MB) and laboratory control sample (LCS) must be analyzed with every analytical batch. Depending on client/project/program specifications, there will also be an LCS duplicate (LCSD) or a matrix spike (MS) and MS duplicate (MSD) pair. Recoveries shall be compared to laboratory generated QC limits or client/program specified limits for all surrogates, MS/MSD, and/or LCS/LCSD spike injections.

10. CALCULATIONS AND DATA ANALYSIS AND REDUCTION

10.1. Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the response of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area or height of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), and is also known as a relative response factor in other methods.

10.1.1. Internal standards are recommended in method 8270D. These internal standards are: 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12. The use of MS detectors makes internal standard calibration practical because the masses of the internal standards can be resolved from those of the target compounds even when chromatographic resolution cannot be achieved.

10.1.2. Internal standard solutions are prepared at two different concentrations: 40 µg/mL for all PAH SIM analyses (Table 1) and 100 µg/mL for SIM analyses of all other analytes listed in Tables 2 through 4.

10.1.3. The volume of the solution spiked into the calibration standards and sample extracts is such that minimal dilution occurs (e.g. 5 µL of solution added to a 500 µL results in only a negligible 0.1% change in the final volume, which can be ignored in the calculations).

10.1.4. The mass of each internal standard added to each sample extract must be the same as the mass of the internal standard added to each calibration standard.

10.2. For each of the initial calibration standards, calculate the RF values for each target compound relative to one of the internal standards as follows;

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

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 in µg/mL.
C_{is} = Concentration of the internal standard in µg/mL.

10.3. Linear calibration using the average response factor:

10.3.1. Response factors are a measure of the slope of the calibration relationship and assume that the curve passes through the origin. Under ideal conditions, the factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected.

10.3.2. To evaluate the linearity of the initial calibration, calculate the mean (average) RF, the standard deviation (SD), and the relative standard deviation (RSD).

Mean RF = $\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$

SD = $\sqrt{\sum_{i=1}^{n} \frac{(RF_i - \overline{RF})^2}{n-1}}$

RSD = $\frac{SD}{\overline{RF}} \times 100$

Where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5
SD = Standard deviation

10.3.3. It is also recommended that a minimum response factor for most common target compounds be demonstrated for each individual calibration level as a means to ensure that the compounds are behaving as expected (see Table 12).

10.3.4. If the RSD of any target analytes is ≤ 20%, then the RF is assumed to be constant over the calibration range and the average RF may be used for analyte quantitation. This is accomplished by re-arranging the equation from section 10.2 above.

$C_S = \frac{A_s \times C_{is}}{A_{is} \times \overline{RF}}$

Where:
$\overline{RF}$ = Average Response Factor
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 in µg/mL
C_{is} = Concentration of the internal standard in µg/mL

10.4. Linear calibration:

10.4.1. If the RSD of the calibration factor is greater than 20% over the calibration range, then linearity though the origin cannot be assumed. If this is the case, the analyst can employ a regression equation that does not pass through the origin. This approach can also be employed based on the past experience of the instrument response. The regression will produce the slope and intercept terms for a linear equation in the form:

$y = mx + b$

Where:

y = instrument response (peak area or height)
m = slope of the line
x = concentration of the calibration standard
b = the y-intercept

10.4.2. The use of origin (0,0) as a calibration point is not allowed. However, most data systems and many commercial software packages will allow the analyst to "force" the regression through zero. This is not the same as including the origin as a fictitious point in the calibration. It may be appropriate to force the regression through zero for some calibrations, but not when the regression is weighted (SW-846 Method 8000D sec. 11.5.2.1). The use of linear regression cannot be used as a rationale for reporting results below the calibration range.

10.4.3. A linear least squares regression attempts to construct a linear equation of the form: y= mx + b, by minimizing the differences between the observed results (y_i, the response calculated from the constructed equation). The regression equation is:

$y_i' = ax_i + b$

Where:

a = Regression coefficient or the slope of the line
b = y-intercept
y_i' = Predicted (or calculated) response for the i^{th} calibration standard
x_i = Mass of the analyte in the i^{th} calibration standard aliquot

10.4.3.1. The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n}(y_i-y_i')^2$$

10.4.3.2. Where n is the total number of calibration points. The regression calculations attempt to minimize the sum of the squares, hence the name "least squares regression".

10.4.3.3. Weighting the sum of the squares of the differences can significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n} w_i(y_i - y_i')^2$$

Where:

w_i = Weighting factor for the calibration standard (w=1 for unweighted least squares regression
y_i = Observed instrument response (area or height) for the i^{th} calibration standard
y_i' = Predicted (or calculated) response for the i^{th} calibration standard
n = Total number of calibration standards

10.4.3.4. Least Squares Equation (LSQ) weighting method to be used for calculation of least squares regression fits, either 1/x or 1/x2, gives increased importance to smaller concentrations and areas. LSQ weight can be applied to linear, quadratic, and cubic fits only.

10.5. Non-linear Calibration:

10.5.1. In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model can be employed (if permitted by program/project criteria). When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen shall have no more than four parameters, i.e., if the model is polynomial, it can be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

10.5.2. The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches described above. Linear regression employs five calibration standards for the linear model; a quadratic model requires a minimum of six calibration standards. The coefficient of determination (COD) is calculated as follows:

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - Y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2}$$

Where:

y_{obs} = Observed response (area) for each concentration of the calibration curve
y = Mean observed response from the initial calibration
Y_i = Calculated response at each concentration from the initial calibrations

N = Total number of calibration points (6 points minimum for quadratic equation)
P = Number of adjustable parameters in the polynomial

10.5.3. Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

10.6. Sample Calculations:

10.6.1. The concentration of each analyte in the sample is determined by the computer software. It calculates the amount of compound from the peak area, using the specified calibration model (CF or Linear Regression).

10.6.2. Using the slope (m) and the intercept (b) from this equation, the concentration of the sample (ug/ml) is calculated and appears on the report page following the chromatogram.

10.6.2.1. Water samples:

10.6.2.1.1. $C_S = \frac{(C_c \times V_e \times D)}{V_s}$

10.6.2.2. Soil samples:

$$C_S = \frac{(C_c \times V_e \times D)}{(W \times S)}$$

Where:

C_S = Concentration of sample in µg/L for waters and mg/kg on a dry weight basis for soils
C_c = Concentration from the curve (µg/mL)
V_e = Total volume of sample extract in mL
V_s = Volume of water sample in liters
D = Dilution factor if extract was diluted
W = Weight of wet soil sample in grams
S = Percent solids

11. CALIBRATION AND STANDARDIZATION

11.1. All stock standard solutions are logged in and assigned a laboratory standard number using the LabTrack software. Any subsequent solutions prepared from these stock standards are recorded and uniquely identified in the appropriate LabTrack logbook.

11.2. Stock standards are purchased from vendors who provide certified solutions. Standards are stored according to manufacturer's recommendations, either in a refrigerator (<10°C) or freezer (<0°C) reserved for standard solution storage.

Unopened standard shall have the manufacturer's suggested expiration date. Opened stock standards expire one year or sooner if comparisons with quality control check samples indicate a problem (not to exceed the manufacturer's expiration date).

11.3. Spiking solutions are diluted stock standards used during sample preparation. Spiking solutions expire 6 months from their preparation date or when the stock standard expires, whichever comes first, unless routine analysis indicates a problem. Spiking solutions are stored in the freezer in the prep lab. See Table 10 for preparation details.

11.4. Intermediate standards are diluted stock standards with concentration levels that are manageable for the preparation of working standards. Intermediate standards expire 6 months from their preparation date or when the stock standard expires, whichever comes first, unless routine analysis indicates a problem. Intermediate standards are stored in the same location as their parent stock standards. See Table 11 for preparation details.

11.5. Calibration standards and calibration check standards are prepared from the intermediate standards and expire 6 months from their preparation date or when the stock standard expires, whichever comes first, unless routine analysis indicates a problem. Calibration standards are also stored in the same location as their parent standards. See Table 11 for preparation details.

- 11.5.1. Calibration standards are prepared at a minimum of five concentration levels and are injected directly into the GC/MS.
- 11.5.2. Add 5 µL of the appropriate internal standard to 500 µL of each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards. The concentrations of the target compounds will vary with each calibration standard level. See section 10.1 above for more information about the internal standards.
- 11.5.3. The injection volume is generally between 0.5-2.0 µL and must be the same for all standards and sample extracts.
- 11.5.4. The lowest concentration calibration standard that is analyzed during an initial calibration curve establishes the method's quantitation limit based on the final volume of the sample extract described in the preparative method or employed by the laboratory.
- 11.5.5. QSM requires that the LOQ or the lowest point in the curve, whichever is greater, be used for the reporting limit (RL).

11.6. Using one of the methods in section 10 above, if a correlation of $r \geq 0.995$ ($r^2 \geq 0.990$) (linear, least squares regression), $r^2 \geq 0.990$ (non-linear regression) or RSD ≤ 20% (linear, through the origin) is obtained then the calibration is deemed acceptable.

11.7. The initial calibration verification standard (ICV) (different lot number or manufacturer from the initial calibration standards) is injected following calibration to verify the initial calibration curve. The percent drift of the target compounds must be less than or equal to 20%.

- 11.7.1. It is highly recommended to employ two standards (ICVs) at different concentrations to verify the calibration curve when using non-linear calibration.
- 11.7.2. One standard shall be near the quantitation limit or action limit.
- 11.7.3. The choice of specific standards and concentrations is generally a method or project specific consideration.

12. QUALITY CONTROL

12.1. This SOP is designed to follow a variety of different projects and program requirements. Table 13 is designed to illustrate the control steps and provisions required to adequately produce acceptable data.

12.2. Certified standard solutions, properly maintained instrumentation, and analyst experience are critical elements in producing accurate results. Standards and instrument are continually checked by analyzing certified external performance test samples.

12.3. Initial Demonstration of Capability (IDC) is a technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of four laboratory control spikes in both liquid and solid matrices. After analysis, the analyst determines the average recovery and relative standard deviation (RSD) of the recoveries for each analyte. When program-specific, project-specific, or internal limits for recovery and RSD are not available, the default criteria of 70-130% recovery and 20% RSD are used until internal limits are generated

12.4. In addition, laboratory blind spikes are used to demonstrate analyst capability. A sample of unknown concentration to the primary analyst is created by a second analyst or group leader by spiking a clean matrix. The sample is taken through all preparatory and analytical steps and reported in LIMS. Results must be within established QC limits.

13. DATA ASSESSMENT/ACCEPTANCE CRITERIA FOR QC MEASURES

13.1. If the response for any quantitation ion exceeds the initial calibration range of the GC/MS, the sample extract must be diluted and reanalyzed. Additional internal standards must be added to the diluted extract to maintain the same concentration as in the calibration standards.

13.2. Samples suspected of containing high levels of contamination or samples with known historical data may need to be diluted prior to analysis. Multiple dilutions may be needed to cover the entire working range of the current calibration.

13.3. 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.

- 13.3.1. The reference mass spectrum must be generated by the laboratory using the conditions of this method (SW-846-8270D).
- 13.3.2. The mass spectral library is updated with each new calibration and is continually updated with the mass spectra from CCVs.
- 13.3.3. The characteristic ions from the reference mass spectrum are defined as 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.

13.4. Compounds are identified when the following criteria are met:

- 13.4.1. The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.
- 13.4.2. The relative retention time (RRT) of each compound in each calibration standard agrees within 0.06 RRT units.

13.4.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

13.4.4. Structural isomers that produce very similar spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomeric peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs that are separable by the GC are identified, quantitated and reported as the sum of both compounds by the GC.

13.4.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one compound. 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 of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When compounds co-elute (i.e. only one chromatographic peak is apparent), the identification criteria can be met, but each compound spectrum will contain extraneous ions contributed by the co- eluting compound.

13.5. For samples containing components that are not a part of the normal target list, a library search may be required for the purpose of tentative identification. Tentatively identified compounds (TICs) are needed only when requested or required by a particular project or program. Data system library search routines shall not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Use the following as guidance for reporting TICs:

13.5.1. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) shall be present in the sample spectrum.

13.5.2. The relative intensities of the major ions agree within ± 30%.

13.5.3. Molecular ions present in the reference spectrum shall be present in the sample spectrum

13.5.4. Ions present in the sample spectrum but not in the reference spectrum shall be checked for possible background contamination. They shall also be reviewed for possible co-elution with another compound.

13.5.5. Ions present in the reference spectrum but not in the sample spectrum shall be checked against the possibility of subtraction from the sample spectrum due to background contamination or co-eluting peaks. Some data reduction programs can create these discrepancies

13.6. Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the extracted ion chromatographic profile (EICP). Quantitation is performed by the data system using the internal standard technique. The internal standards used shall be the ones listed in Tables 1 through 4. Quantitation is performed using the RF averages from the initial calibration and not the continuing calibration check (CCV).

13.6.1. Where applicable, the concentration of any non-target compounds (TICs) identified in the sample shall be estimated. The same formulas that are used for target compounds are used with the following modifications: The areas A_x

and A_{is} are from the total ion chromatograms, and the RF for the compound is assumed to be one.

13.6.2. The resulting TIC concentration is reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

13.7. Reporting Quantitative Analysis

13.7.1. When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. Once the standard retention times and mass ions are compared to the sample retention times, the sample data can be reported. Assessments of all spiked and calibration control samples and standards shall also be finalized before reporting the data.

13.7.2. When the analyst has finished processing the analytical batch, the results are electronically transferred to the LIMS system where weight to volume corrections, dilution factors and percent solids adjustments are made. Once the final results have been verified, a checklist (Table 14, FSV 7-01) is filled out and signed confirming that all the data has been thoroughly scrutinized. At this point the data is turned over to another qualified analyst for final validation. The second analyst confirms the results and electronically marks them validated and signs the checklist. Finally, the validated results are made available to the client services personnel in order for the data to be given to the client or appropriate agencies.

13.7.3. An electronic copy of the data is then filed and archived. The package includes: the sequence run log, checklist, bench sheet copy (Table 15, FSV 7-02), the LIMS run log, verification of calibration data and chromatograms/quant reports. Each sequence file header is labeled with the date of sequence.

14. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

See QAM Appendix 9.

15. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

See QAM Appendix 9.

16. DATA RECORDS MANAGEMENT

16.1. Records are stored for a minimum of 5 years in accordance with the Quality Manual.

16.2. See SOP QA 003 for specifics on document control.

17. WASTE MANAGEMENT

All waste is handled in accordance with CT Laboratories Waste SOP (WS001).

18. REFERENCES

18.1. CT Laboratories Quality Assurance Manual, current revision.

18.2. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.1, DoD QSM, January 2017 or most recent revision.

18.3. USEPA, SW-846, Method 8000D, Rev. 4, July 2014.

18.4. USEPA, SW-846, Method 8270D, Rev. 5, July 2014.

19. FIGURES

19.1. **Table 1: SIM PAH Compound List**

Peak #	Compound	Retention Time (min.)	Relative Retention Time	Primary Ion	Secondary Ion	Code: S=Surrogate I=Internal Standard T=Target Compound	Associated Internal Standard
1	Naphthalene-d8	3.389	0.000	136		I	
2	Naphthalene	3.603	1.004	128	102,74	T	Naphthalene-d8
3	2-Methylnaphthalene-d10	4.050	1.128	152	122	S	Naphthalene-d8
4	2-Methylnaphthalene	4.072	1.135	142	115,89	T	Naphthalene-d8
5	1-Methylnaphthalene	4.137	1.153	141	115,89	T	Naphthalene-d8
6	Acenaphthene-d10	4.787	0.000	164		I	
7	Acenaphthylene	4.686	0.979	152	76,126	T	Acenaphthene-d10
8	Acenaphthene	4.805	1.004	154	126,76	T	Acenaphthene-d10
9	Fluorene	5.167	1.079	166	139,82	T	Acenaphthene-d10
10	Phenanthrene-d10	5.822	0.000	188		I	
11	Phenanthrene	5.837	1.003	178	152,89	T	Phenanthrene-d10
12	Anthracene	5.874	1.009	178	152,89	T	Phenanthrene-d10
13	Fluoranthene-d10	6.659	1.144	212	208	S	Phenanthrene-d10
14	Fluoranthene	6.668	1.145	202	101,88	T	Phenanthrene-d10
15	Chrysene-d12	7.684	0.000	240		I	
16	Pyrene	6.828	0.889	202	101,88	T	Chrysene-d12
17	Benzo(a)anthracene	7.676	0.999	228	200,114	T	Chrysene-d12
18	Chrysene	7.706	1.003	228	114,200	T	Chrysene-d12
19	Perylene-d12	9.034	0.000	264		I	
20	Benzo(b)fluoranthene	8.624	0.955	252	126,113	T	Perylene-d12
21	Benzo(k)fluoranthene	8.654	0.958	252	126,113	T	Perylene-d12
22	Benzo(a)pyrene	8.971	0.993	252	126,113	T	Perylene-d12
23	Indeno(1,2,3-cd)pyrene	10.347	1.145	276	138,137	T	Perylene-d12
24	Dibenz(a,h)anthracene	10.374	1.148	278	139,138	T	Perylene-d12
25	Benzo(g,h,i)perylene	10.626	1.176	276	138,137	T	Perylene-d12

19.2. **Table 2: Pest SIM Compound List**

Peak #	Compound	Retention Time (min.)	Relative Retention Time	Primary Ion	Secondary Ion	Code: S=Surrogate I=Internal Standard T=Target Compound	Associated Internal Standard
1	Naphthalene-d8	3.012	0.000	136		I	
2	Nitrobenzene-d5	2.654	0.881	82	128	S	Naphthalene-d8
3	Acenaphthene-d10	4.444	0.000	164		I	
4	2-Fluorobiphenyl	3.737	0.841	172	171	S	Acenaphthene-d10
5	Propachlor	5.309	1.195	120	176	T	Acenaphthene-d10
6	Desisopropylatrazine	5.659	1.273	158	173,145	T	Acenaphthene-d10
7	Desethylatrazine	5.765	1.297	172	187,145	T	Acenaphthene-d10
8	Phenanthrene-d10	7.248	0.000	188		I	
9	Simazine	6.660	0.919	201	186,173	T	Phenanthrene-d10
10	Atrazine	6.758	0.932	200	215,173	T	Phenanthrene-d10
11	Acetochlor	8.337	1.150	162	146,223	T	Phenanthrene-d10
12	Metribuzin	8.386	1.157	198	57,144	T	Phenanthrene-d10
13	Alachlor	8.561	1.181	160	188,146	T	Phenanthrene-d10
14	Cyanazine	9.853	1.359	225	198,172	T	Phenanthrene-d10
15	Metolachlor	9.591	1.323	162	238,146	T	Phenanthrene-d10
16	Chlorpyrifos	9.678	1.335	197	97,257	T	Phenanthrene-d10
17	Pendimethalin	10.648	1.469	252	162,192	T	Phenanthrene-d10
18	Chrysene-d12	13.914	0.000	240		I	
19	Terphenyl-d14	12.628	0.908	244	122	S	Chrysene-d12

19.3. **Table 3: SIM DNT Compound List**

Peak #	Compound	Retention Time (min.)	Relative Retention Time	Primary Ion	Secondary Ion	Code: S=Surrogate I=Internal Standard T=Target Compound	Associated Internal Standard
1	Naphthalene-d8	7.314	0.000	136		I	
2	Nitrobenzene-d5	5.908	0.808	82		S	Naphthalene-d8
3	Acenaphthene-d10	11.253	0.000	164	63	I	
4	2,6-Dinitrotoluene	10.955	0.974	165	63	T	Acenaphthene-d10
5	2,5-Dinitrotoluene	11.499	1.022	165	63	T	Acenaphthene-d10
6	2,3-Dinitrotoluene	11.693	1.039	165	63	T	Acenaphthene-d10
7	2,4-Dinitrotoluene	11.883	1.056	165	63	T	Acenaphthene-d10
8	3,5-Dinitrotoluene	12.091	1.074	182	63	T	Acenaphthene-d10
9	3,4-Dinitrotoluene	12.464	1.108	182	63	T	Acenaphthene-d10

19.4. **Table 4: SIM 1,4-Dioxane Compound List**

Peak #	Compound	Retention Time (min.)	Relative Retention Time	Primary Ion	Secondary Ion	Code: S=Surrogate I=Internal Standard T=Target Compound	Associated Internal Standard
1	1,4-Dichlorobenzene-d4	4.304	0.000	152	115	I	
2	1,4-Dioxane-d8	2.232	0.519	96	64	S	1,4-Dichlorobenzene-d4
3	1,4-Dioxane	2.250	0.523	58	88	T	1,4-Dichlorobenzene-d4

19.5. **Table 5: PAH SIM MS Parameters**

Group	Compounds	Start Time	m/z
1	Naphthalene-d_8 Naphthalene	3.00	74,102,128,136
2	2-Methylnaphthalene-d10 2-Methylnaphthalene 1-Methylnaphthalene	3.90	89,115,122,141,142,152
3	Acenaphthylene Acenaphthene-d10 Acenaphthene	4.50	76,126,152,154,164
4	Fluorene	5.00	165,166
5	Phenanthrene-d10 Phenanthrene Anthracene	5.50	89,152,178,188
6	Fluoranthene-d10 Fluoranthene Pyrene	6.30	88,101,202,208,212
7	Chrysene-d12 Benzo(a)anthracene Chrysene	7.30	114,200,228,240
8	Perylene-d12 Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene	8.20	118,126,252,264
9	Indeno(1,2,3-cd)pyrene Dibenz(a,h)anthracene Benzo(g,h,i)perylene	9.60	137,138,139,276,278

19.6. **Table 6: Pest SIM MS Parameters**

Group	Compounds	Start Time	m/z
1	Naphthalene-d8 Nitrobenzene-d5	2.20	82,128,136
2	Acenaphthene-d10 2-Fluorobiphenyl	3.50	164,171,172
3	Propachlor	5.00	120,176
4	Desisopropylatrazine Desethylatrazine	5.60	145,158,172,173,187
5	Simazine Atrazine	6.20	173,186,200,201,215
6	Phenanthrene-d10	7.20	188
7	Acetochlor Metribuzin Alachlor	7.80	57,144,146,160,162, 172
8	Cyanazine Metolachlor Chlorpyrifos	9.10	97,146,162,172,197, 198,225,238,257
9	Pendimethalin	10.50	162,252
10	Chrysene-d12 Terphenyl-d14	11.50	122,240,244

19.7. **Table 7: DNT SIM MS Parameters**

Group	Compounds	Start Time	m/z
1	Naphthalene-d8 Nitrobenzene-d5	1.50	82,152
2	Acenaphthene-d10 2,6-Dinitrotoluene 2,5-Dinitrotoluene 2,3-Dinitrotoluene 2,4-Dinitrotoluene 3,5-Dinitrotoluene 3,4-Dinitrotoluene	4.75	63,164,165,182

19.8. **Table 8: 1,4-Dioxane SIM MS Parameters**

Group	Compounds	Start Time	m/z
1	1,4-Dichlorobenzene-d4 1,4-Dioxane 1,4-Dioxane-d8	1.80	58,64,88,96,152

19.9. **Table 9: DFTPP Tuning Criteria**

Mass	Ion Abundance Criteria
51	10-80% of Base Peak
68	<2% of mass 69
70	<2% of mass 69
127	10-80% of Base Peak
197	<2% of mass 198
198	Base peak, or > 50% of mass 442
199	5-9% of mass 198
275	10-60% of Base Peak
365	>1% of mass 198
441	Present by < 24% of mass 442
442	Base peak, or > 50% of mass 198
443	15-24% of mass 442

19.10. **Table 10: DFTPP, Internal Standard, Surrogate, and Spike Solution Preparation Details**

Standard Solution Description	Stock Standard Identity	Stock Standard Concentration (µg/mL)	Stock Standard Volume (µL)	Solvent	Final Volume (mL)	Final Concentration (µg/mL)
DFTPP Tuning Solution	GC/MS Tuning Mix (DFTPP)	500	250	Methylene Chloride	5	25
DFTPP Tuning Solution	GC/MS Tuning Mix (DFTPP)	500	500	Methylene Chloride	5	50
8270 SIM Internal Standards (non-PAH)	Semi-Volatiles Internal Standard Mix	2000	50	Methylene Chloride	1	100
PAH SIM Internal Standards	Semi-Volatiles Internal Standard Mix	2000	20	Methylene Chloride	1	40
PAH SIM Surrogate Solution	PAH SIM Surrogate Mix	2000	20	Acetone	100	0.4
PAH SIM Spiking Solution	Semi-Volatiles PAH Standard Mix	2000	50	Acetone	100	1
8270 SIM Surrogate Solution (non-PAH)	8270 B/N Surrogate Mix	5000	50	Acetone	250	1
Pest SIM Spiking Solution	MDA Pest Mix	500	100	Acetone	50	1
DNT SIM Spiking Solution	2,5-Dinitrotoluene	100	250	Acetone	50	0.5
	3,5-Dinitrotoluene	100	250			
	2,3-Dinitrotoluene	1000	25			
	2,4-Dinitrotoluene	1000	25			
	2,6-Dinitrotoluene	1000	25			
	3,4-Dinitrotoluene	1000	25			
1,4-Dioxane Surrogate Solution	1,4-Dioxane-d8	10000	50	Methanol	50	10
1,4-Dioxane Spiking Solution	1,4-Dioxane	2000	250	Methanol	50	10

19.11. **Table 11: Intermediate and Calibration Standard Preparation Details**

Standard Solution Description	Parent Standard Identity	Parent Standard Concentration (µg/mL)	Parent Standard Volume (µL)	Solvent	Final Volume (mL)	Final Concentration (µg/mL)
DNT SIM ICAL Stock	2,5-Dinitrotoluene	100	250	Methylene Chloride	5	5
	3,5-Dinitrotoluene	100	250			5
	3,4-Dinitrotoluene	1000	25			5
	2,3-Dinitrotoluene	1000	25			5
	2,4-Dinitrotoluene	1000	25			5
	2,6-Dinitrotoluene	1000	25			5
	8270 B/N Surrogate Mix	5000	5			5
DNT SIM ICV Stock	2,5-Dinitrotoluene	100	250	Methylene Chloride	5	5
	3,5-Dinitrotoluene	100	250			5
	3,4-Dinitrotoluene (2nd Source)	1000	25			5
	2,3-Dinitrotoluene (2nd Source)	1000	25			5
	2,4-Dinitrotoluene (2nd Source)	1000	25			5
	2,6-Dinitrotoluene (2nd Source)	1000	25			5
	8270 B/N Surrogate Mix	5000	5			5
DNT SIM ICAL PT 1	DNT SIM ICAL Stock	5	4	Methylene Chloride	1	0.02
DNT SIM ICAL PT 2			10			0.05
DNT SIM ICAL PT 3			20			0.10
DNT SIM ICAL PT 4			100			0.50
DNT SIM ICAL PT 5			200			1.00
DNT SIM ICAL PT 6			300			1.50
DNT SIM ICAL PT 7			400			2.00
DNT SIM CCV			100			0.50
DNT SIM ICV 1	DNT SIM ICV Stock	5	100	Methylene Chloride	1	0.50
DNT SIM ICV 2	DNT SIM ICV Stock	5	300	Methylene Chloride	1	1.50
1,4-Dioxane ICAL Stock Standard	1,4-Dioxane	2000	50	Methylene Chloride	10	10.00
	1,4-Dioxane-d8 (surrogate)	10000	10			10.00
1,4-Dioxane ICV Stock Standard	1,4-Dioxane (2nd Source)	1000	100	Methylene Chloride	10	10.00
	1,4-Dioxane-d8 (surrogate)	10000	10			10.00
1,4-Dioxane ICAL PT 1	1,4-Dioxane ICAL Stock Standard	10	10	Methylene Chloride	1	0.10
1,4-Dioxane ICAL PT 2			20			0.20
1,4-Dioxane ICAL PT 3			50			0.50
1,4-Dioxane ICAL PT 4			100			1.00
1,4-Dioxane ICAL PT 5			150			1.50
1,4-Dioxane ICAL PT 6			200			2.00
1,4-Dioxane ICAL PT 7			250			2.50
1,4-Dioxane CCV			100			1.00
1,4-Dioxane ICV 1	1,4-Dioxane ICV Stock Standard	10	100	Methylene Chloride	10	1.00
1,4-Dioxane ICV 2	1,4-Dioxane ICV Stock Standard	10	200	Methylene Chloride	10	2.00

Standard Solution Description	Parent Standard Identity	Parent Standard Concentration (µg/mL)	Parent Standard Volume (µL)	Solvent	Final Volume (mL)	Final Concentration (µg/mL)
PAH SIM ICAL Stock Standard	Semi-volatiles PAH Standard Mix	2000	25	Methylene Chloride	10	5
	PAH SIM Surrogate Mix	2000	25			5
PAH SIM ICV Stock Standard	Semi-volatiles PAH Standard Mix (2nd Source)	2000	25	Methylene Chloride	10	5
	PAH SIM Surrogate Mix	2000	25			5
PAH SIM ICAL PT 1	PAH SIM ICAL Stock Standard	5	4	Methylene Chloride	1	0.02
PAH SIM ICAL PT 2			20			0.10
PAH SIM ICAL PT 3			40			0.20
PAH SIM ICAL PT 4			80			0.40
PAH SIM ICAL PT 5			160			0.80
PAH SIM ICAL PT 6			200			1.00
PAH SIM ICAL PT 7			400			2.00
PAH SIM CCV			80			0.40
PAH SIM ICV	Semi-volatiles PAH Standard Mix (2nd Source)	5	80	Methylene Chloride	1	0.40
Pest SIM ICAL Stock	List 1 Pesticide Standard	500	100	Methylene Chloride	10	5
	8270 B/N Surrogate Mix	5000	10			5
Pest SIM ICV Stock	EPA Method 507 Pest Mix	100	250	Methylene Chloride	5	5
	Triazine Standard Mix	100	250			5
	Acetochlor	1000	25			5
	8270 B/N Surrogate Mix	5000	5			5
Pest SIM ICAL PT 1	Pest SIM ICAL Stock Standard	5	4	Methylene Chloride	1	0.02
Pest SIM ICAL PT 2			10			0.05
Pest SIM ICAL PT 3			20			0.10
Pest SIM ICAL PT 4			100			0.50
Pest SIM ICAL PT 5			200			1.00
Pest SIM ICAL PT 6			300			1.50
Pest SIM ICAL PT 7			400			2.00
Pest SIM CCV			100			0.50
Pest SIM ICV 1	Pest SIM ICV Stock	5	100	Methylene Chloride	1	0.50
Pest SIM ICV 2	Pest SIM ICV Stock	5	300	Methylene Chloride	1	1.50

19.12. **Table 12: Recommended Minimum Response Factor**

Compound	Minimum Response Factor (RF)
Naphthalene	0.700
2-Methylnaphthalene	0.400
Acenaphthylene	0.900
Acenaphthene	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
2,6-Dinitrotoluene	0.200
2,4-Dinitrotoluene	0.200
Atrazine	0.010

Criteria

19.13. **Table 13: Method 8270 SIM Quality Control Requirements**

Quality Control Item	Minimum Frequency	Acceptance Criteria	Corrective Action	Additional Comments
Tune/Performance Check (50 ng or less DFTPP)	Prior to ICAL and prior to each 12-hour analysis period	Can be acquired as full scan. Ensure correct mass assignment. DFTPP % relative abundance criteria as specified in Table 9. Pentachlorophenol and Benzidine tailing < 2. DDT breakdown ≤ 20%.	Retune instrument. Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Surrogates (Deuterated Monitoring Compounds (DMCs))	All field and QC samples.	**PAH analysis:** Required surrogates are fluoranthene-d10 and methylnaphthalene-d10. Minimum RRF = 0.40. Use recovery limits of 50-150% until in-house limits can be established for these surrogates. **All other SIM analyses:** use surrogates with similar chemistry to analytes of interest. Recovery limits: 1) use client-specified limits 2) for QSM use LCS criteria 3) use in-house limits.	Reanalyze to confirm results. Correct problem, reprep and reanalyze all samples with failing surrogates if sufficient sample material is available. If sufficient sample material is not available, or if there is obvious chromatographic interference, re-prep and reanalysis may not be necessary. Notify the project manager before proceeding. Qualify failing surrogates with an "S" and discuss in the case narrative and/or on the data checklist.	When PAH-SIM analysis is performed, the laboratory may use the same extract for SIM and full scan analysis if the PAH-SIM specific surrogates are also spiked into the sample prior to extraction.

Quality Control Item	Minimum Frequency	Acceptance Criteria	Corrective Action	Additional Comments
Initial Calibration (ICAL)	Each time the instrument is set up and when compounds in the continuing calibration verification (CCV) do not meet criteria. Must be performed prior to any sample analysis.	Each analyte must meet one of these options: RSD ≤ 20% (QSM 5.1 - if pentachlorophenol is a target analyte, then an RSD ≤ 40% is allowed) or linear least squares regression for each analyte $r^2 \geq 0.99$. **Note:** For QSM 5.0 and below and some non-QSM programs, non-linear calibration (quadratic) is also acceptable, with $r^2 \geq 0.99$.	Correct problem and repeat ICAL. For most programs, flagging is not appropriate. Discuss with project management before qualifying data. Any samples reported from data not meeting these criteria must be qualified with a "Z". Discuss qualification in the case narrative and/or on the data checklist.	Miniumum of five concentration levels required for linear calibration. If non-linear calibration is performed, a minimum of six concentration levels must be analyzed. One calibration point must be at the same concentration as the daily CCV. No samples may be analyzed without an acceptable ICAL.
Retention Time Window (RTW) establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL on days when the ICAL is performed. On days when ICAL is not performed, use the initial CCV. RTs of compounds must be within ± 0.06 RRT units from the RRT of the ICAL midpoint or CCV.	Correct problem, then re-run ICAL.	Calculated for each analyte. RRTs shall be compared with the most recently updated RRTs. Characteristic ions must maximize within one scan of each other. After any maintenance is performed that could affect retention times, RRTs may be updated based on the daily CCV.

Initial Calibration Verification (ICV)	After each ICAL, analysis of a second source standard prior to sample analysis. In the event that non-linear (quadratic) calibration is employed, it will be necessary to run ICVs at 2 different concentrations. (See Table 11)	All reported analytes within ± 20% of true value, unless otherwise specified by the client/project/program. Note: When following QSM 5.1, if pentachlorophenol is an analyte of interest, use ± 50%.	Correct problem. Rerun ICV. If still failing, repeat the ICAL. For most programs, flagging is not appropriate. Discuss with project management before qualifying data. Any samples reported from data not meeting these criteria must be qualified with a "Z". Discuss qualification in the case narrative and/or on the data checklist.	No samples may be analyzed until calibration is verified with a second source.
Continuing Calibration Verification (CCV)	Daily before sample analysis and after every 12 hours of analysis time. QSM 5.0 and above also requires a CCV at the end of the analytical batch run.	Concentration ≤ the concentration of the midpoint calibration standard. All reported analytes within ± 20% of true value, unless otherwise specified by the client/project/program. All reported analytes within ± 50% of true value for CCV at the end of the analytical batch run. Note: When following QSM 5.1, if pentachlorophenol is an analyte of interest, use ± 50% in initial CCV as well.	Immediately analyze two additional consecutive CCVs, if the CCVs both pass then samples may be reported without reanalysis. If either fails, perform corrective actions and reanalyze all associated samples since last acceptable CCV. It may be necessary to perform a new ICAL and then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, the failing analytes are qualified with a "Z" in the associated samples and the data is discussed on the data checklist and in the case narrative. Results may not be reported without valid CCVs. Problem analytes will need to be addressed on a project to project basis.

Quality Control Item	Minimum Frequency	Acceptance Criteria	Corrective Action	Additional Comments
Internal Standards (IS)	Added to all blanks, standards, field samples and QC samples.	Retention time (RT) within 10 seconds of RT for associated CCV standard. On days when an ICAL is performed, used the midpoint standard from the ICAL. Peak area must be within -50% to +100% of the area of the ICAL midpoint standard. Note: Other programs/projects/clients may have their own specific criteria that should be followed as stated in their documents.	Inspect the instrument for malfunctions, make corrections, and reanalyze affected samples. If matrix interference is suspected of causing an issue, dilute sample and reanalyze. If corrective action fails in field samples, the data must be qualified and discussed in the case narrative and on the data checklist.	For QSM 5.1, the internal standard is spiked no greater than 0.4 ng/µL.
Method Blank (MB)	One per prep batch of 20 or less, prior to analysis of any field samples.	For QSM: No analytes detected > 1/2 LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. For most non-QSM: no analytes > MDL, or > 5% of the measured concentration in the sample, or > 5% of the regulatory limit, whichever is greater. Follow criteria of the specific program/project/client.	Reanalyze to determine if instrument or laboratory background contaminatioin was the cause. If method blank is still non-compliant, re-extract and re-analyze blank and associated samples. If no sample remains for re-prepping, or if re-prepped data still contains contamination, qualify analytes in associated samples with a "B" and explain in the case narrative and on the data checklist. For QSM data, if the detect is less than 1/2 the DOD LOQ, no action is required.	Results may not be reported without a valid method blank. Flagging is only appropriate when samples cannot be reanalzyed.

Quality Control Item	Minimum Frequency	Acceptance Criteria	Corrective Action	Additional Comments
Laboratory Control Sample (LCS)	One per prep batch of 20 or less.	For non-QSM work, use client specified or in house limits. For QSM work, use the QSM Appendix C limits. If an analyte is not listed in Appendix C, then use project specified or in house limits.	Correct problem and reanalyze LCS and all associated samples for failed analytes if sufficient sample material is available. If reanalysis cannot be performed, the data must be qualified with a "Q" and explained on the data checklist and in the case narrative. For non-QSM work, if the LCS recoveries are high with no associated positive detects for the failing analytes, then no further action is taken.	Must contain all analytes to be reported. Results may not reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)/Matrix spike duplicate (MSD)	One set per prep batch of 20 samples.	Non-QSM work: Use client/project/program specified recovery and RPD limits, if available, or use in house limits. For QSM work: use the QSM Appendix C LCS recovery limits, if available, or use project specified or in house recovery limits limits if not in Appendix C. For QSM 4.2: RPD ≤ 30% For QSM 5.0: RPD ≤ 20% For QSM 5.1: RPD ≤ 40%	If LCS is acceptable, then report probably matrix interference. Qualify data recovery failures with an "M". For non-QSM sample, if recovery is high and there are no analyte detects in the parent sample, then no flagging is required. Qualify RPD failures with a "Y". Discuss qualified data on the data check list and in the case narrative.	For matrix evaluation only. The data shall be evaluated to determine the source(s) of difference.

Quality Control Item	Minimum Frequency	Acceptance Criteria	Corrective Action	Additional Comments
Quantitative and carryover issues	If the detected concentration of any analyte in a sample exceeds the concentration of that analyte in the highes level calibration standard, the sample must be diluted.	The instrument concentration level of all compounds must be within the range of the calibration curve for all samples. Any sample analyzed immediately after a high level sample must display analyte concentrations of the high level targe compounds less than the RL or greater than 5X the RL.	Dilute the sample to bring analyte concentrations within the range of the calibration curve. If any data is reported with any results over the range of the curve, those results must be qualified with an "X". Any sample displaying concentrations of targe analytes between the RL and 5X the RL that was analyzed immediately after a high level sample must be re-analyzed. If the results do not agree, report only the second analysis.	N/A
Characteristic Ions for MS confirmation	QSM 5.1 requirement only: Must use a minimum of 3 ions.	The relative intensities of the characteristic ions of target analytes agree within 30% of the relative intensities in the reference spectrum and the relative intensities must be > 0. Confirmation requires a S/N ratio ≥ 3 for each quant and confirmation ion.	No data can be reported without MS confirmation. Flagging is not appropriate.	Need 3 structurally significant ions that are logical fragments - not isotopic clusters. Internal standards and surrogates can use fewer than 3 ions.

19.14. Table 14: Method 8270 SIM Analysis Data Review Checklist (FSV7-01 Example)

CT Laboratories
Organic Laboratory Section

8270 SIM Analysis Data Review Checklist

Analytical Run #:		**Independent Reviewer:**	
Sequence Date:		**Date of Review:**	
Analyst/Data Interpreter:		**Approval: Yes No**	

Requirements:	**Acceptance**	**Analyst Review**		**Independent Review**		**Comments-explain each "no" response**
	Criteria	**Yes**	**No**	**Yes**	**No**	**(indicate reference to an attachment if necessary)**
INITIAL CALIBRATION (ICAL)						
Was the initial calibration performed using a minimum of five standard concentration levels (six levels for non-linear calibration)?	Lowest standard at or near MRL					
Were the standards used for the ICAL uniquely identified?	standard number					
Was there a DFTPP standard analyzed prior to the ICAL? (see DFTPP section below for acceptable tune criteria)						
Was an instrument blank analyzed prior to the ICAL?						
Were linearity acceptance criteria met for all surrogates and analytes of interest? Note: QSM 5.1 does not allow non-linear (quadratic) calibration.	RSD≤ 20%, linear least squares regression r^2>0.990, non-linear r^2>0.990.					
INITIAL CALIBRATION VERIFICATION (ICV)						
Was there a second source ICV for all target analytes analyzed after the initial calibration and prior to analysis of any samples? Note: If non-linear calibration is used, then it will be necessary to run ICVs at two different concentrations.	Second source					
Was each ICV uniquely identified?	standard number					
Was the recovery for each analyte within QC limits?	± 20%, unless otherwise specified by project/client/program					
CONTINUING CALIBRATION VERIFICATION (CCV)						
Were CCVs for target analytes analyzed at the beginning of the sequence and after every 12 hours? Note: QSM 5.0 and above also requires a CCV at the end of the analytical batch.	Concentration ≤ concentration of the mid-point ICAL standard					
Was each CCV uniquely identified?	standard number					
Was the recovery for each analyte within QC limits?	± 20%, unless otherwise specified by project/client/program Ending CCV (if applicable) ± 50%					
Additional Comments:						

CT Laboratories
Organic Laboratory Section
Analytical Run #:

8270 SIM Analysis Data Review Checklist

Requirements:	Acceptance Criteria	Analyst Yes	Analyst No	Independent Yes	Independent No	Comments-explain each "no" response (indicate reference to an attachment if necessary)
DFTPP						
Was a DFTPP tune check ran at the beginning of every sequence and after every 12 hours?						
Were the relative abundance criteria met?						
Was the peak tailing acceptable for Pentachlorophenol and Benzidine?	Tailing Factor < 2					
Was the breakdown of DDT to DDD and DDE acceptable?	≤ 20%					
BLANKS						
Was method blank (MB) analyzed prior to the analysis of samples?						
Did MB results meet the required criteria?	QSM-the greater of the following: < 1/2 RL, < 1/10 amount in sample, or < 1/10 regulatory limit Non-QSM: < MDL, < 5% amount in sample, or < 5% regulatory limit					
Was a MB prepped and analyzed at a frequency of one per prep batch?	Batch ≤ 20 samples					
LABORATORY CONTROL SAMPLE (LCS)						
Was an LCS analyzed at a frequency of one per prep batch?	Batch ≤ 20 samples					
Were the LCS recoveries within the acceptance criteria?	For QSM: Use Appendix C limits when available; All others, use in-house or client-specified limits					
MATRIX SPIKES						
Was a matrix spike (MS) sample analyzed at a frequency one per prep batch?	Batch ≤ 20 samples					
Were MS recoveries in each MS within the acceptance criteria?	For QSM: Use Appendix C limits when available; All others, use in-house or client-specified limits					

Additional Comments:

CT Laboratories
Organic Laboratory Section
Analytical Run #:

8270 SIM Analysis Data Review Checklist

Requirements:	Acceptance Criteria	Analyst Yes	Analyst No	Independent Yes	Independent No	Comments-explain each "no" response (indicate reference to an attachment if necessary)
LABORATORY CONTROL SPIKE / MATRIX SPIKE DUPLICATE						
Were duplicate spikes (MSD/LCSD) analyzed at a frequency one per prep batch?	Batch ≤ 20 samples					
Were MSD or LCSD recoveries within the acceptance criteria?	QSM Use Appendix C limits when available, else use in-house or client-specified limits					
Is the relative percent difference (RPD) for each analyte between the MS/MSD or LCS/LCSD within the acceptance criteria?	QSM 4.2 ≤ 30%; QSM 5.0 ≤ 20%; QSM 5.1 ≤ 40%; Non-QSM use in-house or client-specified limits					
SAMPLES (INCLUDING BLANKS, STANDARDS, AND QC SAMPLES)						
Are chromatogram characteristics, including peak shapes and areas, consistent with those of the CCV?						
Were the appropriate surrogates used?	PAH vs. non-PAH					
For QSM 5.1 PAH analysis, was the minimum RRF met for each surrogate?	RRF ≥ 0.40					
Are surrogate recoveries for all samples, blanks, standards, and QC samples within acceptance criteria?	QSM 5.1 PAH 50-150%; Other QSM use Appendix C limits; else use in-house or client-specified limits					
Were all samples having analytes detected in amounts exceeding the calibration range diluted and reanalyzed?						
Were all samples extracted within holding times and analyzed within hold time?	Analysis within 40 days of extraction					
Did the samples require additional cleanup steps? (i.e. GPC or sulfur cleanup)	GPC, Sulfur cleanup					
RECORDS AND REPORTING						
Have all data files and relative QC forms been pdf'd?						
Do all chromatograms contain analysis date, time, and analyst initials?						
Are results exceeding acceptance criteria qualified and recorded in the NCR?						
Do the raw reports match the LIMS data?						
Is the ICAL method referenced on the raw data?						

Additional Comments:

19.15. Table 15: SVOC 8270 Extraction Bench Sheet (FSV6-02 & FSV7-02 example)

Method 8270-SV GC/MS Extraction Bench Sheet

(SOP Reference #'s SV006 & SV007)

3510=WATER
3546=Microwave

Prep Batch #:	
Prep Method:	
Analyst:	
Date:	
Start Time:	
End Date:	
End Time:	

Matrix: _____
Balance Used: _____
Ave MW temp(°C): _____

Reagent Lots>>>
Sodium Sulfate _____
Diatomaceous Earth _____
Dionex Solution _____
Methylene Chloride _____
Acetone _____
Sulfuric Acid _____
Sodium Hydroxide _____

Initial Concentration By: _____
Date: _____
GPC Cleanup? (yes/no): _____
Date: _____
Final Concentration By: _____
Date: _____

Microwave Cell #	Sample ID	Comments	(Solids) Sample Weight (g)	(Liquids) Sample Volume (L)	Final Volume (mL)	ph Adj. <2 (Yes/No)	pH Adj. >12 (Yes/No)
		(MB)					
		(LCS)					
		(MS) Parent Sample					
		(MSD)					

MB=Method Blank, LCS=Laboratory Control Sample, MS=Matrix Spike & MSD=Matrix Spike Duplicate

MS/MSD/ LCS Spike Amount (mL): _____ Surrogate Spike Amount (mL): _____
Spike Concentration (µg/mL): _____ Surrogate Spike Conc. (µg/mL): _____
Spike Reference #: _____ Surrogate Spike Reference #: _____

Relinquished to: _____
Date: _____

Reviewed By: _____
Date: _____

19.16. **Table 16: Description of SOP Changes**

Revision Number	Description of Changes	Date
1.0	Reformatted to meet laboratory SOP format criteria. Updated all standards, tables, and requirements to reflect actual lab procedure and to meet new QSM 5.1 requirements. Removed prep information and made reference to prep SOPs.	4/27/2018

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STANDARD OPERATING PROCEDURE

SV 021 Microwave Extraction of Semi-Volatiles Solid Samples

Review Date: 05/28/2019

05/29/2019

Technical Review by: Date

05/29/2019

Approved by: Quality Assurance Date

Table of Contents

1. SCOPE OF APPLICABILITY

1.1. This method describes the procedures for extracting semi-volatile organic compounds from soils, sediments, sludges, and other solid wastes and materials using microwave energy and is designed to follow the guidelines established by EPA SW-846 method 3546. Microwave energy produces elevated temperature and pressure conditions in closed sample vessels containing extraction solvent and achieves recoveries that are equivalent to those achieved by Soxhlet extraction.

1.2. This method is applicable to the extraction of organochlorine pesticides, PCBs, substituted phenols, PAHs, petroleum products, and other semi-volatile organic compounds. This method may also be applicable to the extraction of additional target analytes, provided that adequate performance can be demonstrated for these compounds.

2. SUMMARY OF METHOD

2.1. Samples are prepared for extraction by chemically drying them with sodium sulfate and/or diatomaceous earth and using a metal spatula or a disposable wooden stick to mechanically reduce them to a free flowing powder.

2.2. The sample, any surrogate or spiking solutions, and extraction solvent are added to the 75 mL extraction vessel, sealed, and shaken.

2.3. The vessels are heated to 110°C and held there for 15 minutes.

2.4. The vessels are allowed to cool before opening and proceeding to the concentration step.

3. DEFINITIONS

3.1. For definitions of many of the terms applicable to this SOP, see the Glossary located in the Quality Assurance Manual (QAM).

3.2. Quality Assurance Manual (QAM): a document describing the organization and general operations of a laboratory.

3.3. For a list of common acronyms and abbreviations, see the Acronyms list immediately following the Table of Contents in the QAM.

4. HEALTH AND SAFETY

4.1. The use of organic solvents and other hazardous chemicals, elevated temperatures, high pressures, and exposure to unknown sample contaminants present health and safety concerns.

4.2. Gloves, safety glasses, and other necessary protective clothing shall be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure must utilize appropriate laboratory safety systems.

4.3. The toxicity and carcinogenicity of the chemicals used in this method are not precisely defined. Each chemical and sample shall be treated as a potential health hazard, so care must be taken to prevent undue or extensive exposure.

4.4. The extraction vessels are at elevated temperature and pressure after the extraction stage. Always allow the microwave unit to cycle through the cool down process before

removing the extraction vessels. Once the cool down cycle has finished, the vessels may be removed from the microwave, but they are still slightly warm. Allow the vessels to cool completely to room temperature before opening.

4.5. To prevent the release of solvent vapors into the laboratory atmosphere, ensure that all microwave unit covers are in place, all doors are closed, and the solvent vapor sensor is operational. Replace extraction vessels, plugs, or caps if frequent leaks develop.

5. INTERFERENCES

5.1. Solvents, reagents, glassware, and other sample processing hardware can yield artifacts and /or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Refer to each method for specific guidance on quality control procedures.

5.2. Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

5.3. Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on equipment surfaces, can cause degradation of certain analytes.

5.4. Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interference, further cleanup of the sample will be necessary.

6. EQUIPMENT AND SUPPLIES

6.1. Microwave solvent extraction apparatus (CEM MARS Express or equivalent system).

- 6.1.1. The microwave extraction system must be capable of sensing the temperature to within ± 2.5°C and automatically adjusting the output power within 2 seconds of sensing to maintain the specified average temperature.
- 6.1.2. Temperature sensors should be accurate to within ± 2°C.

6.2. Microwave extraction vessels capable of accommodating at least a 10-g sample size (approximately 75 mL), including vessel plugs, caps, and the vessel carousel for proper seating of vessels in the microwave unit.

- 6.2.1. Vessels must be transparent to microwave energy and inert to reagents and sample components.
- 6.2.2. Vessels must also be capable of withstanding high temperature and pressure conditions.
- 6.2.3. To ensure these specifications are met, it is best to contact the microwave unit manufacturer regarding the purchase of any microwave extraction vessels.

6.3. Microwave extraction vessel cap torque wrench.

6.4. Analytical balance capable of accurately weighing to the nearest 0.01 gram.

6.5. Oven capable of heating to at least 480°C.

6.6. 250-mL glass beakers.

6.7. Glass or polypropylene/PTFE transfer funnels.

6.8. Stainless steel spatulas or disposable wooden craft sticks.

6.9. Syringes, gas tight with PTFE plunger tips.

7. REAGENTS AND STANDARDS

7.1. Sodium sulfate, granular, anhydrous 60/120 mesh, or equivalent. Condition sodium sulfate by heating to 480°C for 4 hours in a shallow glass tray loosely covered with foil. Conditioned sodium sulfate is stored in air tight glass jars.
7.2. Diatomaceous earth.
7.3. Silica sand, hydrocarbon free. Purify by heating to 480°C for 4 hours in a shallow glass tray, loosely covered with foil. Purified silica sand is stored in airtight glass jars.
7.4. Methylene chloride, analyte free, pesticide grade or equivalent.
7.5. Acetone, analyte free, pesticide grade or equivalent.
7.6. Microwave extraction solution, prepared by mixing equal volumes of methylene chloride and acetone. The solution is logged into the semi-volatiles MISC standard logbook and given a unique standard number for tracking purposes.
7.7. Various surrogate and spiking solutions. Refer to the applicable method SOPs to determine the appropriate solutions to be used. Relevant SOPs include:
- 7.7.1. SV001 – Diesel Range Organics (DRO) by GC
- 7.7.2. SV002 – Organochlorine Pesticides by GC Extended Analyte List
- 7.7.3. SV004 – Polychlorinated Biphenyls (PCBs) as Aroclors by GC
- 7.7.4. SV006 – Semi-Volatile Organic Compounds by 8270D
- 7.7.5. SV007 – Semi-Volatile Organic Compounds by GC/MS SIM
- 7.7.6. SV008 – Polynuclear Aromatic Hydrocarbons (PAHs) by HPLC

8. SAMPLE HANDLING AND PRESERVATION

8.1. Solid samples are collected in wide-mouth glass containers with PTFE-lined lids.
8.2. All solid samples are preserved by cooling to ≤6ºC.
8.3. Solid samples must be extracted within 14 days, unless otherwise specified by the client. Solid samples being analyzed for PCBs do not have a method required extraction hold time, but for the sake of consistency in the laboratory, they will also be subjected to the 14 day hold time.

9. PROCEDURE

9.1. Prepare the microwave extraction tubes, caps, and plugs for use by washing them in the dishwasher and thoroughly rinsing with methanol. Dry the tubes upside down in racks and the caps and plugs on foil lined trays until they are completely dry.
9.2. Decant and discard any water layer from the sample. Mix the sample thoroughly with a metal spatula or disposable wooden stick. Discard any foreign objects such as sticks, leaves, and rocks.
9.3. For gummy, fibrous, or oily materials: cut, shred, or otherwise reduce the size of the samples to allow for mixing.
9.4. Weigh approximately 10.00 g of sample to the nearest 0.01 g in a 250-mL beaker and record the final weight on the prep bench sheet (FSV1-02, FSV2-02, FSV2-03, FSV4-02, FSV5-02, FSV6-02, FSV7-02, and FSV8-02). Refer to the applicable method SOPs to determine the appropriate bench sheet.
9.5. Also be sure to record all reagent lot numbers or ID numbers, standard solution ID numbers, analyst initials, times and dates on the prep bench sheet in the spaces provided.

9.6. Use the metal spatula or stick to reduce the particle size of the soil so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Some samples may be too gummy or fibrous to reduce to this size. In these cases, reduce the sample size as much as possible to allow for maximum exposure of the sample surfaces to the extraction solvent.

- 9.6.1. The addition of a drying agent (e.g. sodium sulfate or diatomaceous earth) can make the sample easier to reduce. Start by adding an equal volume of sodium sulfate to the sample and mix well.
- 9.6.2. Add approximately 2.5 g (about 2 scoops) of diatomaceous earth to the sample. Mix well. The sample shall be a free flowing powder.
- 9.6.3. If the sample is not free flowing, add more diatomaceous earth and/or sodium sulfate until the sample has a dry texture. This powder is mixed so that it will allow the sample to pass through a 1 mm sieve.
- 9.6.4. It is important that samples be dried as much as possible, as water will cause uneven heating of the microwave tubes.

9.7. Place the ground sample into a microwave extraction tube using a transfer funnel. There should be a minimum head space of 25%. Record the vessel number next to the sample number on the bench sheet.

- 9.7.1. In the event that samples are very wet and large amounts of drying agent must be used, it may be necessary to reduce the amount of sample being extracted to allow for proper head space in the microwave tubes.
- 9.7.2. Contact project management about very wet samples. Reducing the sample size will alter detection limits and it may become necessary to contact the client before proceeding with the extraction.

9.8. One method blank (MB) and laboratory control spike (LCS) must be prepared with each batch of 20 samples or less. Prepare by adding 10.0 g of sand, and equal volume of sodium sulfate, and approximately 2.5g of diatomaceous earth to a clean 250 ml beaker. Mix and transfer to a microwave extraction tube.

9.9. One sample from each batch of 20 samples or less must be selected for use in the preparation of a matrix spike (MS) and matrix spike duplicate (MSD), unless otherwise specified by the client/program. Select the sample for MS/MSD preparation in the following manner:

- 9.9.1. Choose the sample(s) designated by the client for MS/MSD preparation.
- 9.9.2. If no sample is designated, choose any sample in the batch with sufficient volume for MS/MSD preparation.
- 9.9.3. If there is not enough client sample available to perform an MS/MSD do the following:
  - 9.9.3.1. For all Wisconsin DNR projects, it will be necessary to use a sample received from a previous sampling event to perform the matrix spike analyses. If such a sample is not available, one may be generated from well-mixed garden soil.
  - 9.9.3.2. For non-Wisconsin DNR projects, it will be necessary to prepare a laboratory control sample duplicate (LCSD). The LCSD is prepared in the same manner as the LCS in section 9.8.

9.10. Prepare the MS/MSD as follows:

Transfer approximately 40 grams to a 250 ml beaker. Reduce and mix well with a metal spatula or disposable wooden stick. Weigh out three individual 10.0 grams aliquots of sample (one for the parent sample, one for the MS, and one for the MSD). Dry, reduce, and transfer each aliquot as described above in sections 9.6 and 9.7.

9.11. Add surrogate mix to all client and QC samples using appropriately sized syringes. Place a microwave tube plug on top of each vessel after adding the surrogate as a visual indicator that surrogate has been added.
- 9.11.1. Pesticide and PCB samples receive 0.5 mL of surrogate.
- 9.11.2. 8270D, 8270-SIM, 8015 (DRO/fuel), and 8310 (PAH samples receive 1.0 mL of surrogate.
- 9.11.3. Refer to the applicable analytical method SOPs (SV001, SV002, SV004, SV006, SV007, and SV008) to determine the proper surrogate solution for each sample type being prepared.

9.12. In addition to the surrogate, add the appropriate analyte spiking solution to each LCS, LCSD, MS, and/or MSD. This is best done by removing the plugs from the tubes needing to be spiked and adding the spiking solution to each, replacing the plugs on each tube as the spike is added.
- 9.12.1. Pesticide and PCB samples receive 0.5 mL of analyte spiking solution.
- 9.12.2. 8270D, 8270-SIM, 8015 (DRO/fuel), and 8310 (PAH) samples receive 1.0 mL of analyte spiking solution.
- 9.12.3. Refer to the applicable method SOPs (SV001, SV002, SV004, SV006, SV007, and SV008) to determine the proper analyte spiking solution for each sample type being prepared.

9.13. Add approximately 25 mL of (1:1) methylene chloride: acetone microwave extraction solution to each tube. Re-insert the tube plugs and screw on the caps, making sure they are tight. Torque each cap with the manufacturer-supplied torque wrench.

9.14. Shake each tube for 5-10 seconds. Be sure that all soil is wetted by extraction solvent. The best way to ensure this is to get the entire soil sample to move from one end of the tube to the other and back again several times. If the soil is stuck in the bottom of the tube, it may be necessary to rap the end of the tube on the counter to jar the soil loose.

9.15. Place the extraction tubes in the carousel in the appropriate slots for the number of tubes being used.
- 9.15.1. Less than 16 tubes should be placed evenly spaced in the inside ring.
- 9.15.2. Greater than 16 tubes should be placed evenly spaced in the outside ring. When the outside ring is full, begin spacing the tubes evenly in the inside ring. One carousel holds a total of 40 tubes.
- 9.15.3. There must be a minimum of 8 samples in the carousel to run the microwave. If there are less than 8 samples in the batch, use sand/solvent blanks to make up the shortage. There should never be more sand/solvent blanks than there are actual samples.

9.16. Schedule the CEM Mars with the appropriate method for the number of extraction tubes in the carousel. Use Method 1 for 8-16 tubes; use Method 2 for 17-40 tubes.
- 9.16.1. Extraction cycle, Method 1 for 8-16 samples:
  - 9.16.1.1. Power: 100% at 800 watts
  - 9.16.1.2. Ramp Time: 15 min
  - 9.16.1.3. Temperature: 110°C
  - 9.16.1.4. Hold time: 10 min
  - 9.16.1.5. Cool down cycle: 15 min
- 9.16.2. Extraction cycle, Method 2 for 17-40 samples:
  - 9.16.2.1. Power: 100% at 1600 watts
  - 9.16.2.2. Ramp Time: 15 min
  - 9.16.2.3. Temperature: 110°C
  - 9.16.2.4. Hold time: 10 min

9.16.2.5. Cool down cycle: 15 min

9.17. The microwave cool down cycle cools the tubes so that they may be handled. Tubes must be cooled completely to room temperature before opening them for concentration purposes. Refer to the sample concentration SOP (SV023) for further guidance.

10. CALCULATIONS AND DATA ANALYSIS AND REDUCTION

There are no calculations associated with this extraction procedure. Refer to the individual analytical SOPs for the calculation of final sample results.

11. CALIBRATION AND STANDARDIZATION

11.1. The microwave temperature sensors should have an accuracy of ±2°C.

11.2. The sensor readings are verified quarterly, at a minimum, and should be checked any time a problem is suspected. Such problems may include:

11.2.1. Decreased LCS extraction efficiency.

11.2.2. Increased solvent venting.

11.3. Refer to the CEM Mars Microwave Operation Manual for the procedure on verifying IR sensor temperatures.

11.4. Record the IR sensor temperature verification results in the Microwave Maintenance Logbook.

11.5. If the sensor accuracy is not within ±2°C, it will be necessary to recalibrate the sensors according to the procedure in the CEM Mars Microwave Operation Manual and then re-verify the sensor readings.

11.6. Inability to obtain an acceptable sensor reading shall result in further equipment maintenance.

11.7. Samples cannot be extracted in the microwave without acceptable IR sensor verification readings.

12. QUALITY CONTROL

12.1. Properly maintained instrumentation and analyst experience and expertise are critical elements in producing accurate results.

12.2. Initial Demonstration of Capability (IDC) is a technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of four laboratory control spikes prepared by microwave extraction. After analysis, the analyst determines the average recovery and relative standard deviation (RSD) of the recoveries for each analyte. When program-specific, project-specific, or internal limits for recovery and RSD are not available, the default criteria of 70-130% recovery and 20% RSD are used until internal limits are generated. IDC's are analyzed in the same way as an LCS.

13. DATA ASSESSMENT/ACCEPTANCE CRITERIA FOR QC MEASURES

Not Applicable.

14. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

Not Applicable.

15. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

Not Applicable.

16. DATA RECORDS MANAGEMENT

16.1. An instrument maintenance logbook is maintained for the microwave extraction unit. Upon its completion, it shall be stored for a minimum of 7 years in accordance with the Quality Assurance Manual.

16.2. All electronic bench sheets generated during sample preparation shall also be stored for a minimum of 7 years.

16.3. See SOP QA 003 for specifics on document control.

17. WASTE MANAGEMENT

See QAM Appendix 9.

18. REFERENCES

18.1. USEPA, Method 3546 - Microwave Extraction, Rev. 0, February, 2007.

18.2. USEPA, Chapter 4 – Organic Analytes, Rev. 4, February, 2007.

18.3. USEPA, Method 3500C – Organic Extraction and Sample Preparation, Rev. 3, February, 2007.

18.4. CT Laboratories Quality Manual, current revision.

18.5. CT Laboratories SOP SV001 – Diesel Range Organics (DRO) by GC, current revision.

18.6. CT Laboratories SOP SV002 – Organochlorine Pesticides by GC Extended Analyte List, current revision.

18.7. CT Laboratories SOP SV004 – Polychlorinated Biphenyls (PCBs) as Aroclors by GC, current revision.

18.8. CT Laboratories SOP SV006 – Semi-Volatile Organic Compounds by 8270D, current revision.

18.9. CT Laboratories SOP SV007 – Semi-Volatile Organic Compounds by GC/MS SIM, current revision.

18.10. CT Laboratories SOP SV008 – Polynuclear Aromatic Hydrocarbons (PAHs) by HPLC, current revision.

18.11. CT Laboratories SOP QA003 – Document Control, current revision.

18.12. Department of Defense, *Quality Systems Manual for Environmental Laboratories*, Version 5.1, DoD QSM, March 2017, or most recent revision.

18.13. National Environmental Laboratory Accreditation Conference (NELAC), 2003 *NELAC Standard Chapters 1 to 6*, EPA/600/R-04/003, June 5, 2003 or most recent version.

18.14. ISO. 2005*. General requirements for the competence of testing and calibration laboratories*. ISO 17025

19. FIGURES

Not Applicable.

Revision Number	Description of Changes	Date
0.1	Removed references to method 8270C. Added in LCSD option.	3/3/2017
0.2	Modified MS/MSD/LCS/LCSD options to fit Kansas TPH method requirements. Added references to Kansas methods.	5/23/17
0.3	Updated Kansas TPH method requirements to match updates to the Kansas TPH SOP required by the State of Kansas.	3/1/2018
0.4	Removed references to KS TPH SOP and methods.	5/28/2019

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STANDARD OPERATING PROCEDURE

WC 026 Solids, Total

Review Date: 02/19/18

2/19/18

Technical Review by: Date

03/08/18

Approved by: Quality Assurance Date

Table of Contents

1. SCOPE OF APPLICABILITY

1.1. This SOP is designed to follow procedures and QC requirements outlined in Standard Methods for Determination of Water and Wastewater, Methods 2540B & 2540G and EPA SW-846 method 8000C.

1.2. This method is used to determine the percentage of "Total Solids" (TS) in a sample. It is applicable to sludges, soil, surface water, groundwater, and wastewater (both domestic and industrial).

1.3. This method can also be used in determining the "% Solids" & "% Moisture" content in solid sample matrices for use in dry weight calculations for other analyses.

1.4. The result is given as a percentage of the total weight for sludge and soil samples and as mg/L for surface water, groundwater, and wastewater samples.

2. SUMMARY OF METHOD

2.1. A well-mixed sample is evaporated in a weighed dish and dried to a constant weight in an oven at 103-105 °C. The increase in weight over that of the empty dish represents the total solids.

2.2. The Reporting Limits (RL) for this method is 20mg/L for liquid samples, 0.02 % for sludge samples, and 0.2 % for soil samples.

3. DEFINITIONS

3.1. Duplicate Analysis: Two aliquots of a given sample are analyzed. The difference is then determined from the two results and compared to the laboratory or project specific control limits.

3.1.1. Duplicate at least 10 % of the samples for Total Solids and 5 % of the samples for % Solids.

4. HEALTH AND SAFETY

4.1. Gloves and protective clothing should be worn to protect against unnecessary exposure to possibly hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems (see CTI Health and Safety Manual).

5. INTERFERENCES

5.1. Highly mineralized water, with a significant concentration of calcium, magnesium, chloride and/or sulfate, may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

5.2. Exclude, floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

5.3. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

5.4. The determination of total solids in solid and semisolid materials is subject to negative error due to loss of ammonium carbonate and volatile organic matter during drying. Although this is true also for wastewater, the effect tends to be more pronounced with sediments, and especially with sludges and sludge cakes. The mass of organic matter recovered from sludge and sediment requires a longer ignition time than that specified for wastewaters, effluents, or polluted waters. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem. Make all weighing of samples quickly because wet samples tend to lose weight by evaporation. After drying or ignition, residues often are very hygroscopic and rapidly absorb moisture from the air.

6. EQUIPMENT AND SUPPLIES

6.1. Porcelain, platinum, or high silica glass evaporating dishes or Aluminum weighing dishes.

6.2. Drying oven, capable of 103-105 °C (Fisher, Isotemp 500 series or equivalent).

6.3. Top Loading balance, capable of weighing to 0.01 g (used for soil samples). Entris, Model 2202-1S or equivalent.

6.4. Analytical balance, capable of weighing to 0.0001 g (used for liquid and sludge samples). Ohaus Voyager Pro, Model VP214CN or equivalent.

6.5. Scoop or spatula.

6.6. Wide-bore pipettes.

6.7. Desiccator, provided with a desiccant containing a color indicator of moisture. Drierite (Calcium carbonate) or equivalent.

7. REAGENTS AND STANDARDS

7.1. There are no special standards or reagents required with this analysis.

8. SAMPLE HANDLING AND PRESERVATION

8.1. Samples are collected in resistant-glass or plastic bottles or 4 oz jars, providing that the material in suspension does not adhere to container walls.

8.2. Samples are stored in a refrigerator at 4±2°C unit until analysis.

8.3. Samples analyzed following Standard Methods 2540B & 2540G shall be analyzed within 7 days.

9. PROCEDURE

9.1. If only total solids are requested, heat clean aluminum dishes to 103 – 105 °C for 1 hour. If sample also needs total volatile solids, use a porcelain, platinum, or high silica glass evaporating dish that has been ignited at 500° ± 50 °C for one hour.

9.2. Transfer sample (amount specified below) to a pre weighed dish, and weigh both dish and sample. Record weight.

9.2.1. For soil samples: utilizing the top loading balance, transfer 5-10 g of well mixed sample to a weigh dish, with a scoop or spatula.

9.2.2. For water samples: utilizing the analytical balance, transfer 25-100 mL of well mixed sample to weigh dish, with a pipette. NOTE: If the sample contains suspended solids, it is may be necessary to use a wide-bore pipette.

9.2.3. For sludge samples: utilizing the analytical balance, transfer 10-50 g of well mixed sample to dish. NOTE: If the sludge is a liquid, stir to homogenize before transferring aliquot. If the sludge is a solid, pulverize to homogenize the sample before transferring to the weigh dish.

9.3. Place the dish into an oven at 103-105 °C, dry overnight (at least 8 hrs.).

9.4. When drying is complete, the samples shall be removed from the oven, cooled in a desiccator, weighed back and reported.

9.4.1. A second reading on a selected sample is taken and must agree with the initial reading within 4 % or 50 mg (whichever is less).

9.4.2. If the second reading does not meet criteria place all samples back into the oven for 1 hour and repeat procedure 9.4.1 until acceptable results are obtained.

10. CALCULATIONS AND DATA ANALYSIS AND REDUCTION

10.1. For solid and sludge samples, use the spreadsheet FWC26-03, FWC26-04 or FWC26-05.

10.2. For liquid samples, use the spreadsheet FWC26-02.

10.3. Sludge & Soil Samples (%):

$$\textit{Total Solids / \% Solids} = \frac{(A - B) \times 100}{(C - B)}$$

$$\textit{\% Moisture} = 100 - \frac{(A - B) \times 100}{(C - B)}$$

Where:
A = Dry weight of sample and dish, g
B = Tared weight of dish, g
C = Weight of sample and dish, g

10.4. Water Samples (mg/L):

$$\textit{Total Solids (mg/L)} = \frac{(A - B) \times 1000}{\textit{Sample Vol., mL}}$$

Where:
A = Weight of dried residue + dish, mg
B = Weight of dish, mg

10.5. Precision – Relative Percent Difference (RPD):

$$\textit{\% RPD} = \frac{(\textit{sample conc.} - \textit{dup conc.})}{\{(\textit{sample conc.} + \textit{dup conc.}) / 2\}} \times 100$$

11. CALIBRATION AND STANDARDIZATION

11.1. Follow manufacturer's instructions to calibrate the balances.

12. QUALITY CONTROL

12.1. Duplicate analysis for Total Solids shall be done for every 10 % of samples per matrix. The Relative Percent Difference (RPD) for the duplicates must be less than or equal to the control limits (Figure 1). If the result of the replicate exceeds the quality control limit corrective action must take place. Corrective action shall include reanalysis of affected samples or qualifying the results back to the last acceptable quality control check, unless the laboratory determines the sample results are unaffected (in this case, the rationale must be noted along with the data package).

12.2. A duplicate is needed for every 20 samples requiring % Solids/Moisture analyses and also must be within established control limits.

12.3. Calibration of the analytical balance prior to use will ensure accurate measurements.

12.4. Weighing the sample to constant weight ensures that the sample is not gaining moisture once removed from the oven.

12.5. Properly used equipment, and analyst experience and expertise are critical elements in producing accurate results. Equipment performance is continually checked and documented in instrument logbooks.

12.6. Proper equipment maintenance is another means to ensure adequate method performance.

12.7. Initial demonstration of capability (IDC) is another technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of 4-5 laboratory control samples. After analysis, the analyst calculates the relative standard deviation (RSD) between the analyses. In general “Total Solids results shall agree within 5 %.

13. DATA ASSESSMENT/ACCEPTANCE CRITERIA FOR QC MEASURES

13.1. When the preparation of an analytical batch has been completed, the samples are analyzed and prepared for reporting. The analyst will review the data to ensure QC is acceptable and that exceedances are addressed. Acceptable data is then captured into the LIMS system.

13.2. After data has been captured by LIMS, it is reviewed by the analyst for accuracy and completeness.

13.3. Once the analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

13.4. After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

13.5. A paper hard copy of the data is then filed or archived. The package includes any checklists, the sequence run log, the prep batch, and a copy of the bench sheet (FWC26-(2-5)), the LIMS run log, and verification of calibration data.

14. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

14.1. See QAM.

15. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

15.1. See QAM

16. DATA RECORDS MANAGEMENT

16.1. Records are stored for a minimum of 5 years in accordance with the Quality Manual.

16.2. See SOP QA 003 for specifics on document control.

17. WASTE MANAGEMENT

17.1. See the Quality Assurance Manual (QAM).

18. REFERENCES

18.1. CT Laboratories Quality Manual, current revision

18.2. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.1, DoD QSM, January 2017 or most recent revision.

18.3. National Environmental Laboratory Accreditation Conference (NELAC), 2003 *NELAC Standard Chapters 1 to 6*, EPA/600/R-04/003, June 5, 2003 or most recent version.

18.4. ISO. 2005*. General requirements for the competence of testing and calibration laboratories*. ISO/IEC 17025:2005.

18.5. SM 2540B & 2540G- 1992

18.6. SM 2540B & 2540G- 2011

18.7. USEPA, SW-846, Method 8000C, Rev. 3, March, 2003.

18.8. SM 2540E-2011

19. FIGURES

19.1. Figure 1: Summary of Quality Control Requirements

QC Type	Frequency	Acceptance Criteria	Corrective Action if Unacceptable
Sample Duplicate (DUP)	1 per 10 samples for TS, 1 per 20 sample for % Solids or % Moisture	In-house derived or client/project specific limits: Default: RPD ≤ 5%	Investigate problem, if system precision in control qualify results, if system precision out of control reanalyze entire batch
Constant Weight Sample (Second weighing)	Check one (1) per 10 samples per batch	Weigh until constant weight of or until the weights agree within 4% or 50 mg.	Place back in oven and repeat weighing process until constant weight is achieved
Capability demonstration sample (IDC)	Four (4-5) prepared samples analyzed one time prior to any sample analyses	In-house determined criteria for acuracy and precision	Repeat until acceptable

19.2. Figure 2: Total Solids Data Validation Checklist (FWC26-01, Example)

FORM #: FWC26,27-01
Rev. #: 1.1
Effective Date: 03/01/2017
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Total Solids & TVS Data Validation Checklist

LIMS #:	Method: Total Solids SM2540B&G / Percent Solids SW846-5030A / Total Volatile Solids SM2540G			
Analysis Date	Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved
				Yes ... No

Instructions: Complete one checklist per *analytical run*. Enter the appropriate response for each question. Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

Requirement:	Acceptance Criteria	Analyst Review		Independent Review		Comments: (indicate reference to an attachment if necessary)
		Yes	No	Yes	No	
1. Were samples analyzed within hold time?	7 days					
2. Were samples dried overnight?	> 8hours					
3. Were drying start and stop times recorded?	---					
4. Were duplicates analyzed at the appropriate frequency?	1 per 10 of similar matrix					
5. Were the duplicates within acceptable limits?	Within in house QC limits					
6. Are all samples on the job lists accounted for?	---					

19.3. Figure 3: Total Solids & TVS in Liquids Spreadsheet (FWC26-02, Example)

	FWC26,27-02 Total Solids & Total Volatile Solids in Liquids						TS Run #	TVS Run #				
	Date:			Analyst:						Method: SM2540B		
	Sample ID#	Dish#	DF	Tare Wt. g (E)	Vol ml (F)	Dry Wt. g (G)	Ignited Wt g (H)	Total Solids mg/L	Vol. Solids mg/L		Flags	Comments
1			1					#DIV/0!	0.00			
2			1					#DIV/0!	0.00			
3			1					#DIV/0!	0.00			
4			1					#DIV/0!	0.00			
5			1					#DIV/0!	0.00			
6			1					#DIV/0!	0.00			
7			1					#DIV/0!	0.00			
8			1					#DIV/0!	0.00			
9			1					#DIV/0!	0.00			
*10			1					#DIV/0!	0.00			
dup 10			1					#DIV/0!	0.00			
	* 2nd Reading,		* 2nd Reading,			Average:	#DIV/0!	0.00				
	mg Difference	0.00	mg Difference	0.00		TS RPD=	#DIV/0!		*2nd reading must be within			
						TVS RPD=	0.0%		0.5 mg of the 1st reading			
11			1					#DIV/0!	0.00			
12			1					#DIV/0!	0.00			
13			1					#DIV/0!	0.00			
14			1					#DIV/0!	0.00			
15			1					#DIV/0!	0.00			
16			1					#DIV/0!	0.00			
17			1					#DIV/0!	0.00			
18			1					#DIV/0!	0.00			
19			1					#DIV/0!	0.00			
*20			1					#DIV/0!	0.00			
dup 20			1					#DIV/0!	0.00			
	* 2nd Reading,		* 2nd Reading,			Average:	#DIV/0!	0.00				
	mg Difference	0.00	mg Difference	0.00		TS RPD=	#DIV/0!		*2nd reading must be within			
Balance: Voyager Pro						TVS RPD=	0.0%		0.5 mg of the 1st reading			
Start Time:								Calculations				
Stop Date:								TS, mg/L [(G-E) X 1000] / (F/1000)		TVS, mg/L [(G-H) X 1000] / (E/1000)		
Stop Time:												
			DF correction calculated in LIMS									

19.4. Figure 4: Total Solids (Percent) Spreadsheet (FWC26-03, Example)

	FWC26-03 TOTAL SOLIDS (PERCENT)				LIMS #:	
Start Date:		**Start Time:**			**Analyst:**	
	Sample ID#	**Dish#**	**Tared Weight g *(D)***	**Wet Weight g *(E)***	**Dry Weight g *(F)***	**RESULTS % TOTAL SOLIDS**
1)						0.0%
2)						0.0%
3)						0.0%
4)						0.0%
5)						0.0%
6)						0.0%
7)						0.0%
8)						0.0%
9)						0.0%
10)						0.0%
11)						0.0%
12)						0.0%
13)						0.0%
14)						0.0%
15)						0.0%
16)						0.0%
17)						0.0%
18)						0.0%
19)						0.0%
*20)						0.0%
Dup 20)						0.0%
Dry Weight = Sample + Dish (gms)				* 2nd Reading,		
Wet Weight = Sample + Dish (gms)					Set RPD:	0%
			Balance: XD-2200			
					*mg Difference	0
	Stop Date:					
	Stop Time:			Calculations		
*2nd reading must be within 50mg of the 1st			% Total Solids = ((*F-D*)/(*E-D*))*100			
		RPD, % = Absolute value of... ((Sample-Dup % TS)/(Average%TS))*100				

19.5. Figure 5: Total Solids (Percent) & TVS Sludge Spreadsheet (FWC26-04, Example)

FORM #: FWC26,27-04
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Effective Date: 03/01/2017

Total Solids (Percent) and Total Volatile Solids					LIMS (%TS) #:		LIMS (TVS) #:			
Start Date		Method: SM2540B			Analyst:					
	Sample ID#	Dish#	Tare Wt. g (D)	Sample Wet Wt. g (E)	Dry Wt. g (F)	Total Solids %	Ignited Wt. g (H)	Vol Solids gVS/ gTS	Matrix Type sludge (sl) soil (s)	Flags/ Comments
1						0.00		0.0000		
2						0.00		0.0000		
3						0.00		0.0000		
4						0.00		0.0000		
5						0.00		0.0000		
6						0.00		0.0000		
7						0.00		0.0000		
8						0.00		0.0000		
9						0.00		0.0000		
10						0.00		0.0000		
Dup 10						0.00		0.0000		
*	2nd Reading,		2nd Reading,		Average:	0.00	Average:	0.00		
	Total Solids	0.00	Vol. Solids	0.0000						
	mg Difference	0.00	mg Difference	0.00						
			TS RPD=	0%	TVS RPD=	0%				
11						0.00		0.0000		
12						0.00		0.0000		
13						0.00		0.0000		
14						0.00		0.0000		
15						0.00		0.0000		
16						0.00		0.0000		
17						0.00		0.0000		
18						0.00		0.0000		
19						0.00		0.0000		
*20						0.00		0.0000		
Dup 20						0.00		0.0000		
*	2nd Reading,		2nd Reading,		Average:	0.00	Average:	0.00		
	Total Solids	0.00	Vol. Solids	0.0000			Calculations			
	mg Difference	0.00	mg Difference	0.00			%TS=	(F-D) X 100 / (E-D)	gVS/gTS=	(F-H) / (F-D)
			TS RPD=	0%	TVS RPD=	0%				
2nd Reading must be within 50 mg of the 1st		Balance Used: WCB01								
	Start: Time:		Stop Date:		Stop Time:					

Page 1 %TSTVS1 TS TVS Slg Template_FWC26,27-04

19.6. Figure 6: Total Solids & TVS Percent Moisture Spreadsheet (FWC26-05, Example)

FORM #: FWC26,27-05
Rev. #: 1.1
Effective Date: 03/01/2017

	Total Solids (%) Total Volatile Solids and % Moisture				LIMS #:						
Date:		Method: SM2540B			Analyst:				(% Moisture ?):		
	Sample ID#	Dish#	Tare Wt. g (D)	Sample Wet Wt, g (E)	Dry Wt. g (F)	Total Solids % (G)	Ignited Wt. g (H)	Vol Solids gVS/ gTS	Matrix Type sludge (sl) soil (so)	% Moisture	Comments
1						0.0%		0.0000		100.0%	
2						0.0%		0.0000		100.0%	
3						0.0%		0.0000		100.0%	
4						0.0%		0.0000		100.0%	
5						0.0%		0.0000		100.0%	
6						0.0%		0.0000		100.0%	
7						0.0%		0.0000		100.0%	
8						0.0%		0.0000		100.0%	
9						0.0%		0.0000		100.0%	
*10						0.0%		0.0000		100.0%	
Dup10						0.0%		0.0000		100.0%	
*	2nd Reading,		2nd Reading,			TS Average:	0.0%				
	Total Solids	0.00	Vol. Solids	0.00							
	mg Difference	0	mg Difference	0							
			TS RPD=	0.0%	TVS RPD=	#DIV/0!					
11						0.0%		0.0000		100.0%	
12						0.0%		0.0000		100.0%	
13						0.0%		0.0000		100.0%	
14						0.0%		0.0000		100.0%	
15						0.0%		0.0000		100.0%	
16						0.0%		0.0000		100.0%	
17						0.0%		0.0000		100.0%	
18						0.0%		0.0000		100.0%	
19						0.0%		0.0000		100.0%	
*20						0.0%		0.0000		100.0%	
Dup20						0.0%		0.0000		100.0%	
*	2nd Reading,		2nd Reading,			TS Average:	0.0%				
	Total Solids	0.00	Vol. Solids	0.00				Calculations			
	mg Difference	0	mg Difference	0			%TS =	(F-D) X 100	gVS/gTS=	(F-H)	
			TS RPD=	0.0%	TVS RPD=	#DIV/0!		(E-D)		(F-D)	
2nd Reading must be within 50 mg of the 1st		Balance Used: WCB01					% M =	100% - G			
	Start: Time:		Stop Date:		Stop Time:						

%TSTVS%M 1 Page 1 of 1 TS TVS %Moisture template_FWC26,27-05

19.7. Description of Changes

Revision Number	Description of Changes	Date
04	Document changed to incorporated administrative requirements of ISO 17025 and QSM 5.0. Descriptions of changes have not been tracked in previous versions of this document.	04/03/2014
4.1	Up dated Standard Method References	04/01/2016
4.2	Updated duplicate requirements for % Solids to follow SM2540G-2011	03/01/2017

CT LABORATORIES

delivering more than data from your environmental analyses

STANDARD OPERATING PROCEDURE

WC 040 Total Organic Carbon in Soil

Review Date: 05/28/2019

05/28/2019

Technical Review by: Date

05/29/2019

Approved by: Quality Assurance Date

Table of Contents

1. SCOPE OF APPLICABILITY

1.1. This test method is used to determine Total Organic Carbon (TOC) in soils following the USEPA Lloyd Kahn and SW 846-9060A Methods.

1.2. The matrices applicable to this method include soils, sludges, sediments, wastes, and other solid matrices.

1.3. The current calibration range used for this test method is from 0 – 20 mg of total carbon (see Section 11.2.2).

2. SUMMARY OF METHOD

2.1. Organic carbon is measured using a carbonaceous analyzer. The instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is then analyzed by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2. Carbonates and bicarbonates are inorganic forms of carbon and must be separated from the total organic carbon value. The carbonate and bicarbonate are removed by treatment with phosphoric acid prior to combustion.

2.3. Method Detection Limits (MDL's) are determined annually and fall within the range of 250 – 1000 mg/kg.

3. DEFINITIONS

3.1. For a list of definitions on many of the terms applicable to this method, see the Quality Assurance Manual (QAM).

3.2. For a list of common acronyms and abbreviations, see QAM.

4. HEALTH AND SAFETY

4.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonable achievable.

4.2. Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous chemicals and contaminants in samples. All activities performed while following this procedure should utilize appropriate laboratory safety systems.

4.3. The furnace is at 1100 °C. Use caution when inserting and removing crucibles from the furnace and when doing any maintenance on the instrument.

4.4. For pollution prevention information, see QAM.

5. INTERFERENCES

5.1. Inorganic sources of carbon (such as carbonates and bicarbonates) represent interference and must either be removed by acidification prior to analysis or accounted for in the final calculation.

5.2. Volatile organics in sediments may be lost in the decarbonation step resulting in a low bias.

6. EQUIPMENT AND SUPPLIES

6.1. SKALAR, Primacs MCS Solid Sample TOC Module

6.2. SKALAR, Formacs CA16 TOC Analyzer

6.3. TOC Catalyst: SKALAR catalog no. 2CA10319 or equivalent

6.4. Quartz Wool: SKALAR catalog no. 2CA10359 or equivalent

6.5. Ceramic insert tube: SKALAR catalog no. 2SN22254B or equivalent

6.6. Quartz crucibles: SKALAR catalog no. 2CS22003 or equivalent

6.7. Analytical Balance: Ohaus, Model AP 2500 or equivalent

6.8. Drying Oven: Fisher Isotemp Oven p/n 550-50 or equivalent. Set at 75 °C.

6.9. Compressed Oxygen: Ultra high purity grade. Airgas or equivalent.

6.10. Forceps

6.11. For equipment/instrument maintenance, computer hardware and software, and troubleshooting, see QAM.

7. REAGENTS AND STANDARDS

7.1. Reagent water: Milli Q water >10 mega ohms.

7.2. Phosphoric Acid (Fisher catalog number A242SK-212 or equivalent).

7.3. 25 % Phosphoric Acid: Into a 1 L volumetric flask, add 250 mL concentrated phosphoric acid (7.2) and dilute to volume with reagent water (7.1). Store in the cabinet under the TOC analyzer.

7.4. Dextrose: Fisher (Cat. #D16-500 or equivalent).

7.5. Potassium Hydrogen Phthalate or an alternate source of Dextrose: E.M. Science (Cat. # DX0145-11).

8. SAMPLE HANDLING AND PRESERVATION

8.1. Sampling and storage of samples in glass bottles is preferable but plastic is allowable if it does not contribute to TOC content of sample.

8.2. Samples should be stored at 0-6 °C until analysis.

8.3. Hold time for soil and sludge samples is 28 days. Sediment samples have a hold time of 14 days.

9. PROCEDURE

Note: The following procedure outlines only basic steps for setting up and operating the Primacs MCS instrument. For more detailed information on operating the TOC soil module and TOC4Win MCS software, refer to the SKALAR Primacs MCS user manual.

9.1. Start-up:

9.1.1. Turn on the mains to the Formacs instrument and the Primacs MCS soil module.

9.1.2. Set the temperature on the Primacs MCS to 1100 °C.

9.1.3. Open up the valve on the compressed oxygen. The tank should be set to 30 psi.

9.1.4. Enable the Primacs MCS:

9.1.4.1. Open up the ‘HTAccess’ software. Once logged in, select “Connection” and then press “Auto-connect.” When the analyzer settings table pops up, click “Send settings to analyzer.”

9.1.4.2. Put the Formacs analyzer into stand-by mode by clicking the “Settings” tab and then selecting “Stand-By.” Make sure that

the TC/TN temperature is set to 250 °C and the flow is turned off.

9.1.4.3. Click the “View” tab and then select “Control Panel.” Click “Enable MCS.”

9.1.4.4. Close out of the ‘HTAccess’ software.

9.1.5. Open up the ‘TOC4Win MCS’ software. Once logged in, select “Connection” and then press “Auto-connect.” When the analyzer settings table pops up, click “Send settings to analyzer.”

9.2. Sample Preparation:

9.2.1. Weigh approximately 500 mg of sample into a quartz crucible.

9.2.1.1. Mix the sample well so that it is homogenous (for some samples, it may be difficult to obtain a representative portion due to the small amount of sample used).

9.2.1.2. If a sample contains a lot of organic material (leaves, twigs, etc.), weigh up a smaller portion of sample.

9.2.1.3. Record the sample weight and place the crucible in a labeled aluminum weigh pan.

9.2.2. Add several drops of 25 % phosphoric acid to each sample. Samples that contain inorganic sources of carbon will fizz when acid is added to them. Continue adding acid until the sample no longer fizzes.

9.2.2.1. Acid does not need to be added to Dextrose standards.

9.2.3. Place samples into an oven set to 75 °C for approximately 30 minutes.

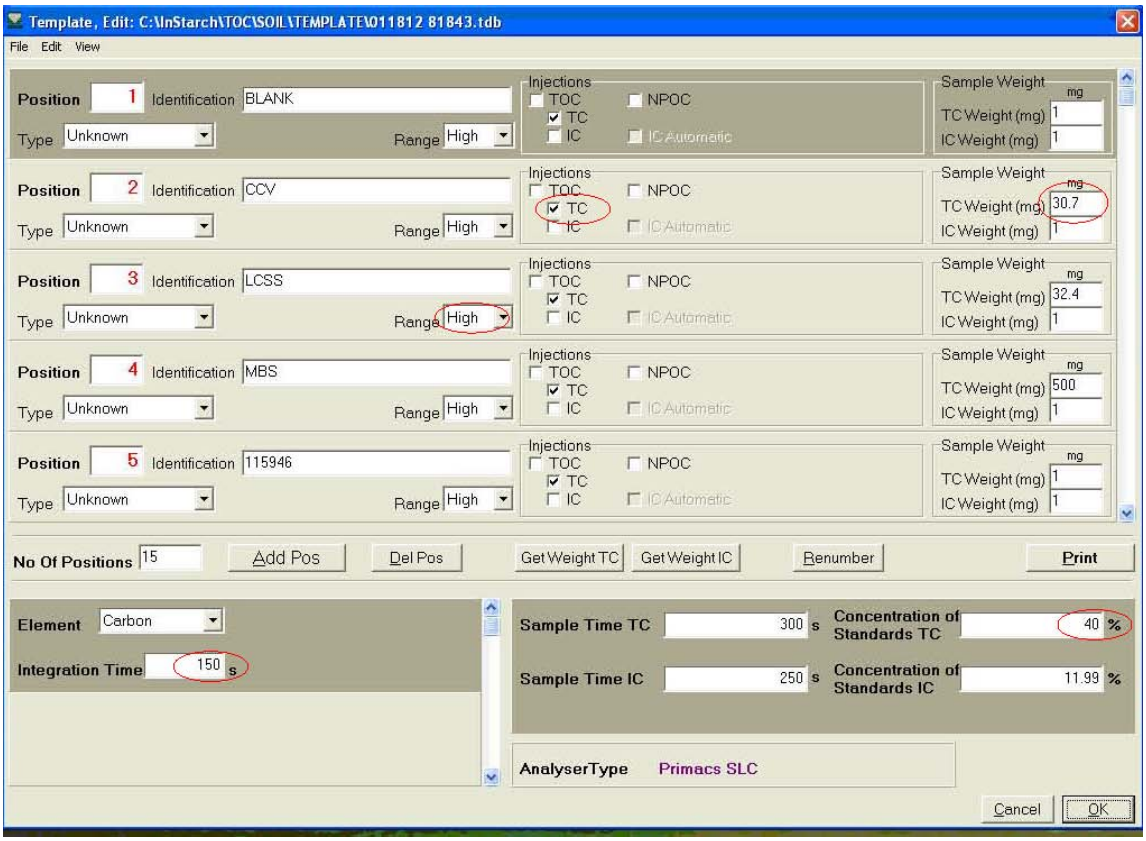
9.3. Run Template Development:

9.3.1. A run template must be created before sample analysis can begin. To make a new template, select the ‘template’ tab and then click ‘new.’

9.3.1.1. For sample analysis, save the template with the date followed by the runs to be analyzed. Example: 021915 112000 112001 112002.

9.3.1.2. For a calibration, save the template with the 'TOC' number for the curve followed by the date analyzed. Example: TOC0001 021915.

9.3.2. There are several key things to look at when creating a new template that are not necessarily default. These items are highlighted in the illustration below:



9.3.2.1. Make sure that you enter the weights of your samples and standards in the 'TC Weight' cell.

9.3.2.2. For the analysis of TOC samples, make sure that the 'TC' box is checked.

9.3.2.3. Make sure that the Range you have selected is the same as it was during the last calibration (for soils, we typically use a 'high-range' calibration).

9.3.2.4. Make sure that the 'Integration Time' is the same as it was on the calibration being used.

9.3.2.5. Enter in the "Concentration of Standards." For Dextrose, the carbon concentration is 40 %.

9.3.3. Add positions to the template that correspond to the QC or samples to be analyzed. The acceptance criteria and the frequency of QC (CCV's, LCS's, MB's, Dup's, etc.) can be found in Figure 1 of this SOP.

9.4. Sample Analysis:

9.4.1. Create a new analysis run by clicking the "Analysis" tab and then selecting "New."

9.4.1.1. Save the analysis the same way as a template (e.g., 021915 112000 112001 112002).

9.4.1.2. Select the template to be used for the sample analysis (this is typically identical to the analysis run).

9.4.2. Select the curve that will be used for sample analysis by clicking "Calibration Curves" in the Results window and then press the "Add Curve" button.

9.4.3. Zero-out the baseline by clicking "AutoZero Carbon" in the Graph Peaks window. Be sure that the baseline is stable before starting sample analysis.

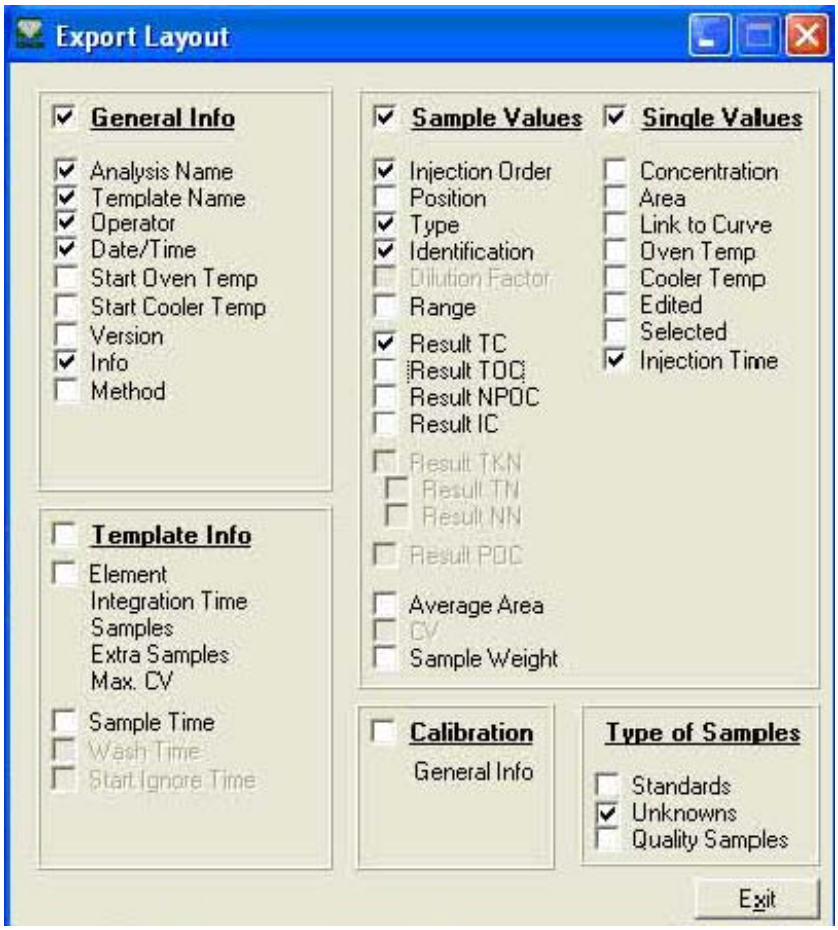
9.4.4. In the "Analysis Info" text box on the Analysis window, type in the 'W' numbers that correspond to the standards being used for analysis.

9.4.5. Click "Start Analysis" when ready to begin analyzing samples.

9.4.6. Add samples to the TOC soil module by following the procedure outlined in the Primacs MCS user manual.

9.5. Shut-down and Data Export:

9.5.1. When the analysis of all samples and QC is complete and the data have been reviewed, export the results to LIMS. This is done by clicking the "Export Results" button on the Analysis window. Each run must be exported individually. The following table illustrates the proper export layout:



9.5.2. Manually set the temperature on the Primacs MCS to 40 °C. Allow the instrument to cool off with flow.

9.5.3. When the instrument is cool, close the valve on the compressed oxygen tank.

9.5.4. Turn off the mains to the Primacs MCS and the Formacs.

9.5.5. Close down the TOC4Win MCS software.

10. CALCULATIONS AND DATA ANALYSIS AND REDUCTION

10.1. *Dry Weight Concentration (mg/kg) = A/B*

Where:

A = Instrument reading for sample (mg/kg)
B = % solids as a decimal

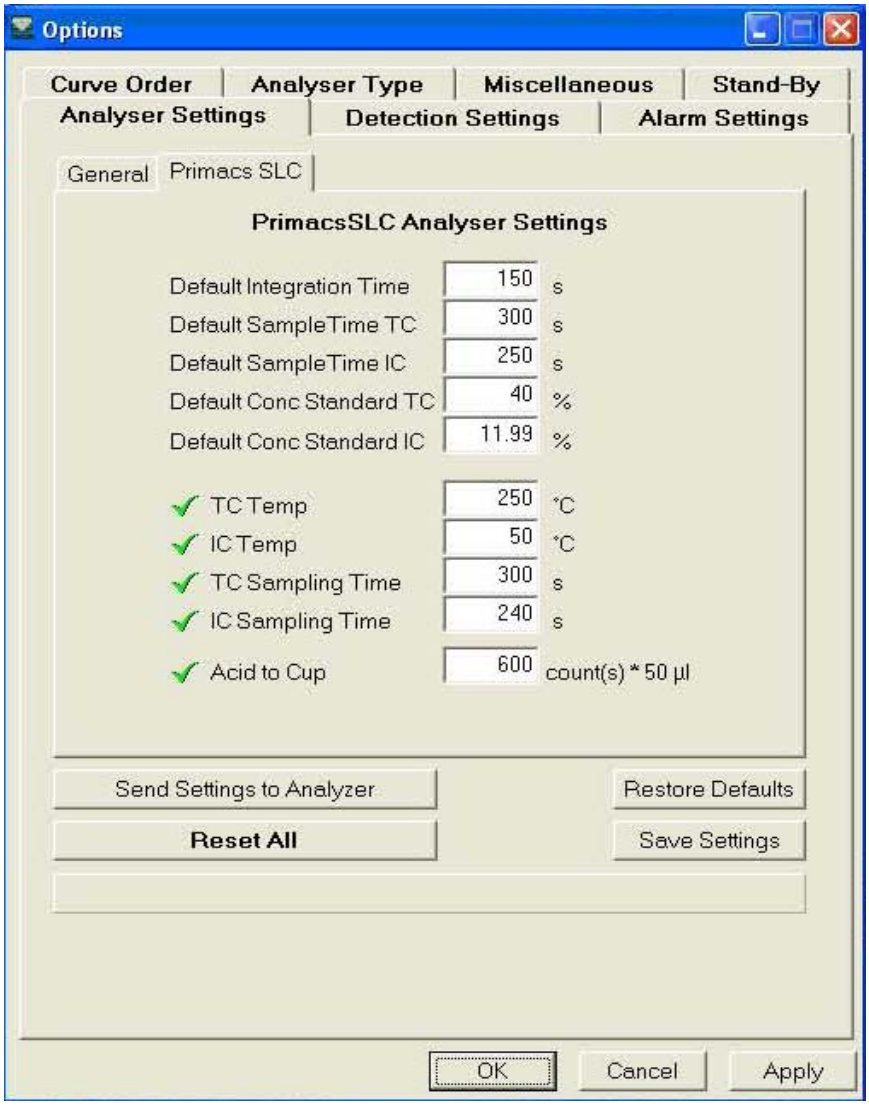
10.2. % RSD = Percent Relative Standard Deviation:

$$\% RSD = \frac{Standard\ Deviation}{Mean} \times 100$$

11. CALIBRATION AND STANDARDIZATION

11.1. To facilitate appropriate peak response and sensitivity, the entire operating system must be correctly set up and maintained before calibration and sample analyses can occur. Using the proper settings and programming will greatly increase the likelihood that calibrations will be acceptable. The manufacturer's recommended settings can be altered to optimize peak shape, reproducibility, and response.

The following table illustrates the settings being utilized currently:



11.2. Calibration Standards – Calibration standards are prepared at a minimum of three concentration levels (although seven levels are currently being used) and are prepared by weighing various amounts of the CCV/Calib. Dextrose standard (Dextrose is 40 % carbon). One of the concentration levels shall be at a concentration near, but above, the detection limit and at or below the reporting limit. The remaining concentration levels shall correspond to the expected range of concentrations found in real samples. The current calibration range for soils is 2 mg to 20 mg carbon (a 'zero' point is also included in the calibration).

11.2.1. Calibration standards are plotted on a curve by the instrument's computer software. Procedures for programming the calibration are outlined in the reference manuals supplied with the Primacs MCS instrument. The plotted curves must have a correlation coefficient (r) of 0.995 or better in order for the curve to be considered valid. Calibration standards are not static and can be altered as long as linearity can still be demonstrated. It is not allowed to remove any internal curve points in order to make a curve acceptable; however, it is acceptable to reanalyze a curve point if initially unacceptable or to remove the highest point if a loss in linearity is demonstrated.

11.2.2. The following table outlines the preparation of a seven level calibration curve for soil samples:

CCV/Calib. Dextrose (mg)*	**Total Carbon (mg)**
0	0
5	2
10	4
20	8
30	12
40	16
50	20

*These are approximate weights.

11.3. A second source ICV is analyzed immediately following a successful calibration. An ICV is prepared by weighing approximately 10 mg of ICV Dextrose. The acceptance criteria for the ICV are outlined in Figure 1 of this SOP.

11.4. An ICB is also analyzed when calibrating the instrument. An ICB is prepared by simply analyzing a blank quartz crucible. The acceptance criteria for the ICB are outlined in Figure 1 of this SOP.

12. QUALITY CONTROL

12.1. This SOP is designed to follow a variety of different projects and programs requirements. Figure 1 is designed to illustrate the control steps and provisions required to adequately producing acceptable data.

12.2. Contract Specific Sample Analysis: For certain samples, limits are specified by the QAPP (Quality Assurance Project Plan) associated with a given project. For these samples follow the limits specified in the QAPP for that project.

12.3. Program Specific Limits: Samples analyzed under the guidance of certain programs; such as the Department of Defense Quality Systems Manual (DoD/QSM) or Louisville Chemistry Guidance (LCG), require their own specified limits. For these samples follow the limits specified in the manuals for that program.

12.4. Per QSM 5.0, LOD and LOQ checks must be analyzed on a quarterly basis (or once per analytical batch for infrequently performed analyses).

12.4.1. LOD checks should be spiked at a concentration at least two times higher than the calculated MDL.

12.4.2. In the absence of set QSM limits, in-house LCS limits are used for acceptable recovery criteria for LOQ checks.

12.5. Initial demonstration of capability (IDC) is another technique used to ensure acceptable method performance. An analyst must demonstrate initial precision and accuracy through the analysis of 4-5 laboratory control spikes for each matrix and sample type. After analysis, the analyst calculates the average recovery (AR) and the relative standard deviation (RSD) of the recoveries for each analyte. In the absence of specific criteria found in the EPA methods or project specific limits, the default criteria of 70-130 % recovery and 20 % RSD are used until internal limits are generated.

12.6. Certified standard solutions and chemicals, properly used instrumentation, and analyst experience and expertise are critical elements in producing accurate results. Standards and instrument performance are continually checked by analyzing external performance test samples provided by the appropriately accredited agencies. Internal blind spikes are also utilized to check analyst performance.

12.7. Proper instrument maintenance is another means to ensure adequate method performance. Refer the Shimadzu TOC 500A Instruction Manual or the Shimadzu Solid Sample Module Instruction Manual as needed.

13. DATA ASSESSMENT/ACCEPTANCE CRITERIA FOR QC MEASURES

13.1. When the analysis of an analytical batch or sequence has been completed, the data is processed and prepared for reporting. The analyst will review the data to ensure QC is acceptable and that exceedances are addressed. Acceptable data is then entered into the LIMS system.

13.2. After data has been entered into LIMS, it is reviewed by the analyst for accuracy and completeness. See checklist (FWC40-01) for data review guidance.

13.3. Once the analyst has reviewed and approved the data, it is given to a peer or supervisor for review.

13.4. After the second reviewer approves the data, the reviewer sends the data to "validated" status in LIMS.

13.5. A paper hard copy of the data is then filed or archived. The package includes the checklist, the sequence run log, and a copy of the bench sheet (if applicable), the LIMS run log, and verification of calibration data.

14. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

See QAM.

15. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

See QAM.

16. DATA RECORDS MANAGEMENT

16.1. Records are stored for a minimum of 5 years in accordance with the Quality Manual.

16.2. See SOP QA 003 for specifics on document control.

17. WASTE MANAGEMENT

See QAM.

18. REFERENCES

18.1. CT Laboratories Quality Manual, current revision

18.2. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.0, DoD QSM, July 2013 or most recent revision.

18.3. Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.1, January 2017 or most recent revision.

18.4. National Environmental Laboratory Accreditation Conference (NELAC), 2003 *NELAC Standard Chapters 1 to 6*, EPA/600/R-04/003, June 5, 2003 or most recent version.

18.5. ISO. 2005*. General requirements for the competence of testing and calibration laboratories*. ISO/IEC 17025:2005.

18.6. Determination of Total Organic Carbon in Sediment (Lloyd Kahn Method), USEPA, July 27, 1988.

18.7. US EPA, SW-846, Method 9060A, Revision 1, November 2004.

18.8. SKALAR Formacs TOC/TN Analyzer User Manual, October 2009.

18.9. SKALAR Primacs MCS TOC add-on module User Manual, January 2011.

19. FIGURES

19.1. Figure 1: Summary of Quality Control Requirements

Procedure	Frequency of Procedure	Acceptance Criteria	Corrective Action if Unacceptable
4 point curve (3 standards and a blank)	Initially and as needed	r ≥ 0.995 for each regression line	Repeat until acceptable
Initial calibration verification (ICV)	Second source standard run after each ICAL and daily prior to sample analysis	%R: 90-110%	Reanalyze ICV standard, if still unacceptable repeat ICAL
Initial calibration blank (ICB)	After each ICV, prior to sample analysis	< RL	Remake and reanalyze CB once, if still unacceptable investigate and correct problem or flag results less than 20 X's the ICB with a 'B' qualifier
Continuing calibration verification (CCV)	Daily, prior to sample analysis, after every 10 analyses, and at end of run	%R: 90-110%	Remake and reanalyze CCV, if still unacceptable investigate and correct problem. Reanalyze all samples after last acceptable CCV.
Continuing calibration blank (CCB)	After each CCV	<RL or <20 times less than the lowest sample result	Remake and reanalyze CB once, if still unacceptable investigate and correct problem then reanalyze all samples after the last acceptable CCB or flag results less than 20 X's the CCB with a 'B' qualifier
Laboratory Control Standard (LCS)	Analyzed with each batch of samples (or at project/program specified frequencies)	With in-house limits Default 80-120 %R.) or within project/program specified limits	Remake and reanalyze LCS once, if still unacceptable investigate and correct problem. Reanalyze all samples associated with failing LCS. IF reanalysis is not possible samples must be "Q" qualified.
Method Blank (MB)	Analyzed with each batch of samples (or at project/program specified frequencies)	< MDL or project/program specified limit. < ½ RL for DoD-QSM	If unacceptable, all associated samples that have detects ≤ 20 times (or project specific) the blank detection and are greater than the MDL must be reanalyzed or 'B' qualified
Matrix Replicate (DUP)	Sample + 3 reps / 20 samples per solids matrix or at project / program frequencies	% RSD within in house limits (Default ±30%) or project/program specified limits	Qualify results with 'Y' flag
Capability demonstration sample (IDC)	Four (4) prepared samples analyzed one time prior to any sample analyses and one blind sample	Within in house limits. Default 70-130% Recovery ±20% RSD or within project/program specified limits	Repeat until acceptable

19.2. Figure 2: TOC in Soil Data Review Checklist (FWC40-01, Example)

		Method: Total Organic Carbon: Lloyd Kahn Method / 9060A		Independent Data Review Checklist		
LIMS Run #(s)	Analysis Date		Analyst / Data Interpreter	Independent Reviewer	Date of Review	Approved? (Yes or No)
						Yes

Instructions: Complete one checklist per *analytical sequence* . Enter the appropriate response for each question.
Each "No" response requires an explanation in the Comments section, and may require the initiation of a Nonconformance Report.

		Analyst Review		Independent Review		Comments:
		Yes	No	Yes	No	(indicate reference to an attachment if necessary)
1. Were the samples acidified prior to analysis and analyzed within hold time?	No effervescence; analyzed within 28 days					If No: Qualify data analyzed after hold time (H).
2. Was the calibration curve performed using the required number of standards?	Minimum of 3 standards and a blank					If No: Recalibrate using required number of standards.
3. Was the correlation coefficient acceptable?	r ≥ .995					If No: Recalibrate.
4. Were the ICV and ICB analyzed?	---					If No: Analyze ICV and ICB prior to any sample analyses.
5. Was the ICV result acceptable?	90 – 110 % Rec. or contract/program specific					If No: Reanalyze, if NO after second analysis, address problem and recalibrate.
6. Was the ICB result acceptable?	< LOD or contract/program specific					If No: address possible contamination and reanalyze.
7. Was an LCS & MB run with each batch of samples?	One each per analytical batch or contract/program specific frequency.					If No: Reanalyze affected samples with appropriate QC.
8. Was the LCS recovery acceptable?	In-house derived or contract/program specific limits.					If No: Reanalyze affected samples with an acceptable LCS when possible, otherwise qualify affected samples (Q).
9. Were the MB results acceptable?	< LOD or project/ program specific (<1/2 RL for DOD-QSM).					If No: Reanalyze affected samples with acceptable MB when possible, otherwise qualify affected samples (B).
10. Were the CCV's analyzed at the required frequency?	Beginning, after every 10 sample, & at the end of a sequence.					If No: Reanalyze affected samples with appropriate CCV intervals.
11. Were the CCB's analyzed at the required frequency?	After each CCV (unless MB analyzed after CCV)					If No: Reanalyze affected samples with appropriate CCB intervals.
12. Were the CCV recoveries acceptable?	90 – 110 % Rec. or project/ program specific					If No: Reanalyze affected samples.

13. Were the CCB results acceptable?	< LOD or project/ program specific					If No: Reanalyze affected samples with acceptable CCB when possible, otherwise qualify affected samples (B).
14. Were all positive results that were reported within the calibration curve?	---					If No: Weigh a smaller portion of sample and reanalyze.
15. Were the appropriate number of samples analyzed in quadruplicate?	1 / 20 of the same matrix or project/ program specific					If No: Prepare and analyze the appropriate number of replicated samples.
16. Was the %RSD on the replicated sample acceptable?	≤ 30%					If No: Qualify the affected parent sample result (Y).
20. Are all samples on the job lists accounted for?	---					If No: Analyze samples that were missed.
21. Is the standards prep log numbers noted on the analytical report?	---					If No: Document the standards used for calibration and analysis.
22. Were post analysis corrections addressed and/or the Audit Trail function turned on (if available)?	Correction should be initialed, dated, and reason given. Audit trail must be on (if available)					If No: Initial, date, and state reason for any changes or corrections.
23. Were non-matrix related nonconformities (if applicable) documented in the NCR spreadsheet?	---					If No: Enter nonconformity information into the NCR spreadsheet before data review/validation.

19.3. Figure 3: TOC % RSD Template (FWC40-02, Example)

Total Organic Carbon (TOC)

Analyst:
Date:
Run #:
Sample #:

Matrix = Solids

% Standard Deviation Calculation: % Std. Dev. = Std Dev./Mean X 100

Sample Result	Dup. 1	Dup. 2	Dup. 3	Mean	Std. Dev.	% Std. Dev.
				0.00	#DIV/0!	#DIV/0!

Limits: 30%

19.4. Figure 4: TOC Soil Bench Sheet (FWC40-03, Example)

TOC SOIL BENCHSHEET

Analyst:		**Method:**	Lloyd Kahn
Run #(s):		**Balance:**	WCB01
Date:		**CCV Std.:**	W23772
Start Time:		**LCS Std.:**	W23192

	Sample ID	Weight (mg)
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29		
30		

Stop Time:	

19.5. Description of Changes

Revision Number	Description of Changes	Date
2	Document changed to incorporated administrative requirements of ISO 17025 and QSM 5.0. Descriptions of changes have not been tracked in previous versions of this document.	03/12/2014
2.1	Document was reviewed, re-formatted, and updated for QSM 5.0.	02/19/2015
2.2	Removed the Final Concentration column in section 11.2.2 and changed the MDL concentration range in section 1.3.	01/06/2016
2.3	Added QSM 5.1 reference.	03/16/2018
2.4	Administrative changes.	05/29/2019

Attachment B
Field Audit Checklist

Field Audit Checklist

Instructions: Review this checklist to ensure field work is conducted as proposed.

Site:	
Field Personnel:	
Date:	

☐ Have daily (morning and night) toolbox safety meetings been conducted?

☐ Have daily emails to project team been sent to help track project status and to keep key Anchor QEA team members up to date with the field program?

☐ Does the on-site field lead have contact information for all subcontractors on site?

☐ Has the laboratory courier been contacted (if needed) to pick up samples at the end of the day? If courier is not being used, has time been allocated to deliver samples to shipping center?

☐ Has the SSP been reviewed and signed by all field personnel and has the work been performed in accordance with theSSP (including proof of certification for all personnel)?

☐ Do any Job Safety Analyses need to be updated?

☐ Have the project FSP, QAPP, and SSP been reviewed by each field team member? Is there a hardcopy of each on site?

☐ Have sampling procedures such as acceptance criteria, sample description homogenization, and decontamination of equipment (particularly for PFAS) been conducted as described in the FSP and QAPP?

☐ Have the duplicate, matrix spike, and matrix spike duplicate samples been collected for sediment and surface water analyses?

☐ Has a rinsate blank been collected for each sampling method?

☐ Have there been any substantial changes from the FSP, QAPP, or SSP?

- ☐ If yes, have the PM, DNR, and EPA been notified?

☐ Is investigation-derived waste being stored, labeled, and tracked properly? Have samples been collected for waste characterization? Are additional drums needed for future sampling?