Memo

SUBJECT
RACER Trust Pontiac North Campus
Initial PFAS Sampling Plan

TO
Peter Ramanauskas, USEPA

DATE
April 18, 2023

DEPARTMENT
Resilience

PROJECT NUMBER
30167840

COPIES TO
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In response to the United States Environmental Protection Agency (USEPA) letter dated November 14, 2022, regarding the potential use of per- and polyfluoroalkyl substances (PFAS) associated with the former operations at RACER Pontiac North Campus (Site), RACER is proposing to sample groundwater at select monitoring well locations for PFAS analysis. The purpose of this sampling is to look for the presence of PFAS and evaluate if any follow-up activity is warranted.

Samples will be collected from 27 monitoring locations across the Site in areas of interest (AOIs) most likely to be impacted in the event PFAS were used during former operations and to provide for general geographic coverage. Historical operations targeted for sampling include wastewater treatment, metal plating and fabrication, and waste storage and piling. Sampling locations are provided in **Table 1** and shown on **Figure 1**.

Procedure

Sampling for PFAS presents unique challenges to typical field sampling protocols as PFAS can be found in many materials such as Teflon tape, pump bladders, and water and oil resistant gear. While most of these materials will not present a large source of contamination of PFAS, they should be considered. Sampling will be conducted in accordance with the Arcadis PFAS Sampling Technical Guidance Information (TGI) to help ensure the chance of cross-contamination is minimized. The PFAS Sampling TGI will be provided to the field staff and is included as **Attachment 1**.

Decisions based on analytical results, potential field sampling errors, and potential laboratory errors will be made by Arcadis technical staff. For this initial scope of work, the objective is to identify potential presence/absence of PFAS that could be used to evaluate an area or areas of the Site for potential investigation and continued sampling. The results of the sampling will be summarized in a report submitted to USEPA and will include proposed additional sampling, as appropriate.

The following procedures will be used when collecting groundwater samples for PFAS at the Site:

Field Personnel Equipment

Due to the ubiquitous nature of PFAS and the potential for cross-contamination field equipment will include the following additional precautions:

- Oil and water-resistant clothing such as Gore-Tex or other outdoor performance wear will not be worn. Sampling attire will include natural fabrics that have been well laundered. Rubber rain gear is acceptable for wet weather sampling.
- New, clean nitrile gloves will be used for each sampling location.
- Showering will be avoided on the day of sampling.
- Use of personal care products will be minimized to those that are medically necessary.
- Any food will be consumed away from the area of sampling. Hands will be washed before resuming sampling.

Groundwater Sample Collection

- Monitoring wells will be gauged for depth to water and total depth prior to sampling. Gauging will be used to verify monitoring well construction and condition (e.g., free of obstructions and/or excessive sediment accumulation). Gauging data will not be used to generate groundwater elevation contour maps. A more complete dataset used to construct contour maps is collected during the PNC annual groundwater sampling event.
- Groundwater samples will be collected from each monitoring well using a submersible pump.
- Low-flow sampling procedures will be used to collect the samples.
    - An example of a standard groundwater sampling log is provided in **Attachment 2**.
- Equipment will be decontaminated between samples in accordance with the PFAS Sampling TGI (**Attachment 1**).
- Samples will be collected near the surface of the water column in the well once low-flow purging is complete.
- Samples will be collected in laboratory supplied HDPE plastic containers.
- Samples will not be filtered.
- Samples will be stored in a cooler with ice at 4^{o} C for transport to the laboratory.
- Samples will be submitted to the laboratory utilizing laboratory provided chain of custody forms (**Attachment 2**).

Sampling Equipment

- All plastic sampling equipment will be HDPE. This applies to passive sampling bags, pump bladders, tubing used for purging, and flow through cells. Sampling equipment will not contain any material that is Teflon coated or is noted to be organic resistant or non-stick.
- Reusable sampling equipment (e.g., flow through cells) will be rinsed with PFAS-free water between sampling locations.
- Appropriate size sample bottles will be provided by the laboratory.
- Equipment will be calibrated at the start of each of day per the manufacturer's calibration procedures and calibration information will be recorded in the field daily log. An example of a field daily log form has been

provided in **Attachment 2**. Manufacturer calibration procedures for the sampling equipment are provided in **Attachment 3**.

Laboratory Analysis

- Groundwater samples will be analyzed by Pace Analytical Services in West Columbia, South Carolina.
- Samples will be analyzed by LC-MS/MS with isotope dilution by modified USEPA Method 537M. The modified method includes analysis of 28 PFAS, including Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) and all other PFAS for which EGLE has a Part 201 Drinking Water Criteria and USEPA has proposed a Maximum Contaminant Level. A complete list of the 28 PFAS is included as **Attachment 4**.
    - The laboratory standard operating procedure (SOP), including the reporting limits for the PFAS compounds, for modified USEPA Method 537M is included as **Attachment 5**.
- Analysis of the entire sample (i.e., whole sample analysis) will be completed.
- Expected laboratory turnaround time for sample analysis is approximately 4 to 5 weeks.

Sampling QA/QC

- Two equipment blanks will be collected with decontaminated sampling equipment.
- Duplicate samples will be collected at a frequency of 1 duplicate sample for every 10 samples (3 total).
- Matrix spike/Matrix spike duplicate (MS/MSD) samples will be collected at a frequency of 1 MS/MSD sample for every 20 samples (2 total).

Sampling will be completed following approval of this sampling plan. Sampling is anticipated to be completed in April 2023; however, the exact date of the sampling event will be contingent on staff availability and will be weather permitting. Results of the sampling will be compared to EGLE Part 201 drinking water and groundwater-surface water interface (GSI) criteria and provided to USEPA as a summary report approximately 4 weeks after receipt of the final laboratory analytical report. All analytical results will be managed using the EQuIS database that currently houses all PNC analytical data. All laboratory analytical reports will be validated by Arcadis staff not associated with the sample collection and data will be reviewed in accordance with USEPA National Functional Guidelines for Organic Superfund Methods Data Review, EPA-540-R-20-005 (November 2020), with reference to the historical USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, OSWER 9240.1-05A-P, October 1999, as appropriate.

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Figure 1 – Proposed PFAS Sampling Locations

Table 1 – PFAS Groundwater Monitoring Plan Summary

Attachment 1 – Arcadis PFAS Sampling Technical Guidance Information

Attachment 2 – Standard Field Forms

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USEPA
April 18, 2023

Attachment 3 – Equipment Manufacturer Calibration Procedures

Attachment 4 – PFAS Compound List

Attachment 5 – Laboratory Standard Operating Procedure for Modified USEPA Method 537M

Figure

Service Layer Credits: Source: Esri, Maxar, Earthstar Geographics, IGN, and the GIS User Community

CITY: NOVI, MI DIV: ENV DB: TRY PIC: PM: TM: TR: PROJECT NUMBER: COORDINATE SYSTEM: NAD 1983 StatePlane Michigan South FIPS 2113 Feet Intl
D:\GIS\Project Files\MotorsLiquidationCompany\PontiacNorthCampus\Documents\Former_Fiero_Property\SiteInvestigation_2021\SiteWidePFASSampling_2023_B.mxd PLOTTED: 4/14/2023 12:49:30 PM BY: TYarbrough

FORMER BUILDING 25
FORMER BUILDING 15
SPO
OFF-SITE GROUNDWATER (COLUMBIA AVENUE)
FORMER FIERO PARKING LOT
FORMER FIERO PLANT 17
GRAND TRUNK LINE
OFF-SITE GROUNDWATER (FIERO)
USPS REGIONAL DISTRIBUTION CENTER
MONTCALM STREET SEEP AREA
SWDF
W-12
HARRIS LAKE
OFF-SITE GROUNDWATER (MFD)
PERRY PARK

LEGEND

- EXISTING MONITORING WELLL
- EXISTING TEMPORARY MONITORING WELL
- PROPOSED PFAS SAMPLING LOCATION
- FIERO BULKHEADING COMPLETED IN 2020
- BULKHEADING COMPLETED IN 2012
- ACTIVE STORM SEWER LINES (FIERO)
- APPROXIMATE LOCATION OF STORM SEWER LINES
- AREA OF INTEREST BOUNDARIES
- CURRENT OR FORMER RACER PROPERTY

0 600 1,200
SCALE IN FEET

RACER TRUST
PONTIAC NORTH CAMPUS
PONTIAC, MICHIGAN

PROPOSED PFAS SAMPLING LOCATIONS

ARCADIS

FIGURE 1

Table

Table 1
Initial PFAS Groundwater Monitoring Plan Summary
April 2023
RACER Trust Pontiac North, Pontiac, Michigan

Well	Gauging	Analyte	Primary Function
		PFAS	
MWM16-30	X	X	Monitoring well located downgradient from former basement sump area that handled metal fabrication waste oil with known vinyl chloride impact
MWM4-05	X	X	Monitoring well located in the northern portion of the Site to identify potential upgradient sources.
MWM16-40	X	X	Monitoring well located downgradient of the AOI M-5 former fill/disposal area.
MWM32-09	X	X	Monitoring well located along the western property boundary to allow for evaluation of potential off-site migration.
MWM30-01	X	X	Monitoring well along the southern property boundary of the former Northern Metal Fabrication Division (NMFD) to evaluate potential off-site migration.
MWM5-02	X	X	Monitoring well located in former disposal area
MWM16-37	X	X	Monitoring well located downgradient of former metal fabrication facility with known vinyl chloride impact
MWM32-01	X	X	Monitoring well located in former pressed metal and hydroform operations area
MWM2-22	X	X	Monitoring well located near former metal plating area with known VOC impact
MWM2-28	X	X	Monitoring well located near former metal plating area with known VOC impact
MW-03-17	X	X	Monitoring well located near seep management system injection well and downgradient from former Plant 8 basement
MWW10-SEN01	X	X	Monitoring well downgradient from several AOIs and known LNAPL impact
MWW1-04	X	X	Monitoring well located along the southwestern property boundary to allow for evaluation of potential off-site migration.
TW-01-03	X	X	Monitoring well in former disposal area and provides general coverage of the Site
TW-MD-01	X	X	Perimeter well located in groundwater seep area, downgradient from former disposal area
SEEP VAULT	X	X	Vault that is collection/discharge point from horizontal drain collecting water from several hundred feet along downgradient perimeter
MWOS-05	X	X	Perimeter well located downgradient of former storm water detention facility
MWW10-04	X	X	Monitoring well located downgradient from a former waste storage pad, AST farm, and plating area
MWF12-01R	X	X	Monitoring well located downgradient from several AOIs including a former waste water treatment plant
MWF12-02R	X	X	Monitoring well located downgradient from several AOIs including a former waste water treatment plant
MWF16-23	X	X	Monitoring well located at downgradient perimeter from several AOIs with known VOC impacts and provides general coverage of the Site
MWF16-06	X	X	Monitoring well located in known VOC source area
MWF16-18	X	X	Monitoring well located in known VOC source area
MWF16-05	X	X	Monitoring well located in known VOC source area
MWF16-26	X	X	Monitoring well located along the Fiero western property boundary to allow for evaluation of potential off-site migration.
MW-02-17	X	X	Monitoring well located along the Fiero southern property boundary to allow for evaluation of potential off-site migration.
MWF8-01	X	X	Monitoring well located upgradient of Fiero portion of the Site to allow for evaluation of possible upgradient contributions

Notes:
PFAS - Per- and polyfluoroalkyl Substances

Attachment 1

Arcadis PFAS Sampling Technical Guidance Information

TGI – Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guide

Rev: 10

Rev Date: January 26, 2022

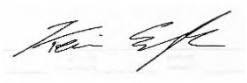
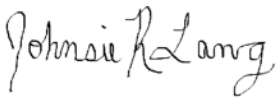
Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
	0	April 27, 2017	All	Initial Release	Erica Kalve Erika Houtz Sue Tauro
	1	June 19, 2018	1 through 4 and 17	Updated Information on Sampling Materials	Erica Kalve Erika Houtz
	2	October 15, 2018	6 to 16	Minor updates on laboratory elements, updates to decontamination procedures, and clarification on equipment and reagent blank collection	Erika Houtz Erica Kalve
	3	December 17, 2018	4, 6, 17	Removed Sharpies from acceptable field writing implements; Changed language in Section 3.2 and Section 10.5 to provide stricter guidance for DoD projects.	Erika Houtz, Erica Kalve
	4	March 26, 2019	4,5	Removed Citranox from acceptable Decon solutions in Table 1a, added all fluoropolymer containing materials to prohibited items in Table 1b. Made a correction that Liquinox contains trace levels of 1,4 Dioxane, not Alconox.	Erika Houtz
	5	October 16, 2020	14	Added Air Force preference to sample surface water at surface for Air Force investigations.	Erika Houtz

	6	March 23, 2021	4, 5, 7, 12, 13, 14, 15, 16, 17	Made clarifications that fine/ultra-fine point Sharpies are allowed. Referenced 2018 MDEQ sampling guidance. Made updates to 'After Sample Collection' in Section 7.	Kevin Engle
	7	April 18, 2021	All	Changed title from Poly- and Perfluoroalkyl Substances to **"Per- and Polyfluoroalkyl Substances"** and changed PFASs to PFAS.	Rosario Varrella, Erika Houtz
	8	May 4, 2021	12, 13, 15, 16	Clarified that sample containers should have an HDPE lined screw cap and that LDPE plastic sheeting should be used.	Kevin Engle, Erika Houtz
	9	October 20, 2021	Note that numbers have shifted one page forward relative to prior versions. 5, 7, 9-12, 15, 16, 18-25.	Specific acceptable sunscreen and insect repellent brands were added to Table 1. Clarified language regarding footwear and H&S trainings. Laboratories section and Section 10.5 was updated to reflect new laboratory names and an updated version of the QSM. Sections 5 and 6 were updated to provide clearer language on health and safety protocols for sunscreen, insect repellent, and rain events. Added language to specify decontamination of reusable equipment prior to initial use in Section 7.1. Section 8 on Waste Management was updated to state that	Kevin Engle, Erika Houtz

				waste storage and disposal should be determined in the site specific workplan. Section 9 was updated to include Rite in the Rain® notebooks as approved for PFAS sampling. Changed the term "sample port" to "sample location" when describing where to place plastic sheeting. Section 10.1 was updated to indicate an equipment blank can be collected for unvetted hazard controls that contact a sample. References were updated to include the newer version of the DoD QSM, MDEQ Sampling Guidance, and California State Water Board PFAS Sampling Guidance.
	10	January 26, 2022	Various, Section 7	TGI formatted to comply with new QMS TGI template and Arcadis brand compliance. Indicated to avoid use of anti-fog spray on safety glasses due to possible presence of PFAS.

Approval Signatures

Prepared by:		1/26/2022
	Kevin Engle, PG Geologist (Preparer)	Date
Reviewed by:		1/26/2022
	Johnsie Lang, PhD (Subject Matter Expert)	Date

1 Introduction

This document is intended to provide guidance to field staff sampling for Per- and Polyfluoroalkyl Substances (PFAS). The content in this document describes the intended use, scope and application, personnel qualifications, equipment, cautions, health and safety considerations, procedures, waste management, data recording and management, and quality assurance of PFAS sampling.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, regulation-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

3 Scope and Application

The purpose of this Technical Guidance Instructions (TGI) is to provide guidance on field sampling to be used for **Per- and Polyfluoroalkyl Substances** (PFAS). This protocol was adapted from various sources including Arcadis Australia, Transport Canada, and the U.S Army Corp of Engineers (USACE) Omaha. In general, sampling techniques used for PFAS site characterization are consistent with conventional sampling techniques used in the environmental industry, but special consideration is made regarding PFAS-containing materials and cross-contamination potential. **Table 1a** provides a summary of materials that have been approved for site investigation; this list is expected to grow longer as industry experience increases. **Table 1b** provides a summary of field equipment and materials that have available testing information and/or industry knowledge regarding

PFAS cross-contamination potential, and it is recommended that these materials be prohibited for sample collection; for materials that are suspected of containing PFAS and/or to retain PFAS, these recommendations are considered preliminary and subject to change. Further discussion of approved and prohibited materials is found throughout this document.

Table 1a: Summary of Acceptable Sampling Equipment and Materials for PFAS Site Investigations

Sampling Materials	Additional Considerations	References
Water Sampling Materials		
High density polyethylene (HDPE) or silicone tubing materials	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
HDPE HydraSleeves™	Low density polyethylene (LDPE) HydraSleeves™ are not recommended	USACE 2016; MassDEP 2017
Drilling and Soil Sampling Materials		
PFAS-free drilling fluids	--	DER 2016
PFAS-free makeup water	Confirm PFAS-free water source via laboratory analysis prior to investigation	--
Acetate liners	For use in soil sampling	USACE 2016
Sample Containers and Storage		
HDPE sample containers with HDPE lined lids for soil and water samples	Laboratory should provide; whole bottle analysis of aqueous samples combined with a solvent rinse of bottle is recommended	DER 2016, MassDEP 2017
Ice contained in plastic (polyethylene) bags (double bagged)	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Field Documentation		
Ball point pens	--	MassDEP 2017
Standard paper and paper labels	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Fine/Ultra-Fine point Sharpies®	Larger point Sharpies® should be avoided.	MDEQ 2018
Decontamination		
Water-only decontamination	Confirm PFAS-free water source via laboratory analysis prior to investigation	DER 2016

Sampling Materials	Additional Considerations	References
Alconox® or Liquinox® followed by deionized water or PFAS-free water rinse	Liquinox® known to contain trace levels of 1,4-dioxane	NHDES 2016; USACE 2016; MassDEP 2017
Methanol, isopropanol, or acetone	Special health and safety precautions are necessary	UNEP 2015; USACE 2016
Sun and Biological Protection		
OFF Deep Woods, Sawyer Permethrin	Apply >10 m away from sampling area	MDEQ 2018
Banana Boat, Coppertone, Neutrogena, Meijer, and L'Oreal Sunscreens	Apply >10 m away from sampling area	MDEQ 2018

Note: This list is considered preliminary and additional materials may be added as additional information becomes available. Project teams are expected to follow a methodical evaluation process of materials to be used and confirm acceptance prior to implementation of field activities.

Table 1b: Summary of Sampling Equipment and Materials Not Recommended for PFAS Site Investigations.

Sampling Materials	Known PFAS-Containing Materials	Suspected PFAS-Containing Materials	Materials with Potential to Retain PFAS	References
Water Sampling Materials				
Teflon®, PTFE-containing or other fluoropolymer coated or containing field equipment (e.g., tubing, bailers, liners, tape, plumbing paste, pump parts)	x			DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Passive diffusion bags			x	MassDEP 2017
LDPE HydraSleeves ™			x	USACE 2016; MassDEP 2017
Water particle filters			x	MassDEP 2017
Drilling and Soil Sampling Materials				
Aluminum foil			x	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Drilling fluid containing PFAS	x	x		DER 2016
Sample Containers and Storage				
Glass sample containers with lined lids			x	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017

Sampling Materials	Known PFAS-Containing Materials	Suspected PFAS-Containing Materials	Materials with Potential to Retain PFAS	References
LDPE containers and lined lids			x	USACE 2016
Teflon® or PTFE- lined lids on containers (e.g., sample containers, rinsate water storage containers)	x			DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Reusable chemical or gel ice packs (e.g., BlueIce®)		x		DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Field Documentation				
Self-sticking notes and similar office products (e.g., 3M Post-it-notes)		x		DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Waterproof paper, notebooks, and labels	x			DER 2016, MassDEP 2017
Markers		x		NHDES 2016
Decontamination				
[Some] detergents and decontamination solutions (e.g., Decon 90® Decontamination Solution)	x	x		DER 2016; NHDES 2016; MassDEP 2017

Note: For materials that are suspected of containing PFAS, or have the potential to retain PFAS, project specific considerations may provide adequate justification for use during the field event. For example, further evaluation may be conducted in the form of pre-field equipment blank sample analysis.

Given the extremely low detection limits associated with PFAS analysis and the many potential sources of trace levels of PFAS, field personnel are advised to err on the side of caution by strictly following these protocols, frequently replacing nitrile gloves, and rinsing field equipment to help mitigate the potential for false detections of PFAS. A summary of other specific items related to field sampling for PFAS are discussed in the sections below.

This TGI applies to all Arcadis and subcontractor personnel involved in field sampling for PFAS.

4 Personnel Qualifications

4.1 Sampling Personnel

Field personnel must have current health and safety training, including 40-hour HAZWOPER training, up to date 8-hour refresher, site supervisor training, and site-specific training, as needed. In addition, field personnel will be versed in the other relevant SOPs (e.g., low flow sampling) and will possess the skills and experience necessary

to successfully complete the desired field work. The site Health and Safety Plan (HASP) and other documents will identify any other training requirements such as site-specific safety training or access control requirements.

4.2 Laboratories

These laboratories are example laboratories that could be used to analyze environmental media for PFAS, pending project approval:

- United States: Pace, SGS, Vista, ALS, and Eurofins
- Canada: AXYS-SGS and Bureau Veritas

Other laboratories may be used if they are appropriately accredited for PFAS analysis according to any project requirements. It is recommended that a laboratory is Environmental Laboratory Accreditation Program (ELAP)-accredited for PFAS analysis in accordance with the Department of Defense (DoD) Quality Systems Manual (QSM) 5.3 Table B-15 or any subsequent updates. **For all data collection efforts at DoD sites, PFAS data must be obtained using a method that is DoD ELAP-accredited under QSM 5.3 or later.**

5 Equipment List

The following equipment and materials must be available for sampling:

- Site plan of sampling locations, relevant work plan (or equivalent), and this TGI;
- Appropriate health and safety equipment, as specified in the site HASP;
- Dedicated plastic sheeting (preferably high-density polyethylene [HDPE]) or other clean surface to prevent sample contact with the ground;
- Conductivity/temperature/pH meter;
- Dissolved oxygen meter, oxidation reduction potential meter, and turbidity meter;
- Depth to water meter;
- If using low-flow groundwater sampling techniques, peristaltic pump (groundwater sampling)/bladder pump (with PFAS free bladder/ HDPE bladder), flow through cell, and accompanying HDPE and silicone tubing;
- Hydrasleeves™, if using Hydrasleeves™ for groundwater sampling;
- Metal trowel for soil samples; specialized soil/sediment sampling equipment as required;
- Brushes for scrubbing sampling equipment;
- Pens, pencils, and/or fine/ultra-fine point Sharpies® for writing;
- Clipboards, field binders, and field note pages that are not waterproof;
- Labeled sample bottles:
    - Water: HDPE bottles fitted with polypropylene screw cap only; some types of PFAS samples (primarily drinking water) may require preservative, which will be indicated by the laboratory conducting the analysis. The laboratory will specify the sample bottle volume.

  - Soil and sediment: HDPE bottles fitted with polypropylene screw cap only; no preservatives. The laboratory will specify the sample bottle volume.
- If high concentrations of PFAS related to class B firefighting foams are expected, bring additional small vials to conduct field-based shaker tests for foaming;
- Ziploc® bags to hold ice and samples;
- Bottles containing “PFAS-free” water used for reagent blanks;
- Labeled, thoroughly decontaminated coolers for samples with ice; Blue ice is not permitted;
- Deionized or distilled water for initial decontamination rinsing;
- “PFAS-free” water provided by the laboratory for final decontamination rinsing;
- Methanol, isopropanol, or acetone if able to be brought safely to field site; especially important for decontamination during soil sampling;
- Alconox or Liquinox®;
- Packing and shipping materials;
- Groundwater and/or Sampling Log; and
- Chain-of-Custody (COC) Forms.

6 Cautions

6.1 Food Packaging

Some food packaging may be treated with PFAS-containing chemicals to prevent permeation of oil and water in the food outside of the packaging. To avoid potential food packaging-related PFAS contact:

- Do not bring any food outside of the field vehicles onsite and eat snacks and meals offsite.
- Wash hands after eating.
- Remove any field garments or outer layers prior to eating. Do not put them back on until done eating and hands are washed.

6.2 Field Gear

6.2.1 Clothing

Many types of clothing are treated with PFAS for stain and water resistance, in particular outdoor performance wear under brand names such as Gore-Tex®. To avoid potential clothing-related PFAS contact:

- Do not wear any outdoor performance wear that is water or stain resistant, or appears to be. Err on the side of caution.

- Wear pre-laundered (multiple washings, i.e., 6+) clothing that is not stain resistant or waterproof (unless made from the materials listed in Section 5).
- Natural fabrics such as cotton are preferred. Synthetic fabrics may also be acceptable if there is no indication on the label that the fabric is water and stain resistant.
- Most importantly, avoid contacting your clothing with sampling equipment, bottles, and samples.

6.2.2 Personal Protective Equipment

Safety Footwear

Some safety footwear has been treated to provide a degree of waterproofing and increased durability and may represent a source of trace PFAS. If at all possible, Gore-Tex footwear should not be worn and safety footwear without waterproofing should be worn; footwear that provides adequate safety from physical hazards is required and takes precedence over potential PFAS concerns. To avoid any PFAS cross contamination to samples from footwear:

- Do not contact your footwear with equipment, bottles, or samples in any way.
- Do not allow gloves used for sampling to come in contact with safety footwear.

Nitrile Gloves

Wear disposable nitrile gloves at all times. Don a new pair of nitrile gloves **before** the following activities at each sample location:

- Decontamination of re-usable sampling equipment;
- Contact with sample bottles or “PFAS-free” water bottles;
- Insertion of anything into the sample ports (e.g., HDPE tubing); and
- Handling of any quality assurance/quality control (QA/QC) samples including field blanks and equipment blanks.

Don a new pair of nitrile gloves **after** the following activities:

- Handling of any non-dedicated sampling equipment;
- Contact with contaminated surfaces; or
- When judged necessary by field personnel.

6.3 Personal Hygiene

- Shower at night.
- Do not use personal care products after showering such as lotions, makeup, and perfumes, UNLESS medically necessary.
- Use sunscreen and insect repellent as necessary for health and safety, i.e., if sampling is to occur outdoors in direct sunlight and/or if insect hazards may be present. Specific products that are acceptable for PFAS

sampling are listed in Section 7.1.1. Apply sunscreen and insect repellent prior to initiating field sampling. If sunscreen and/or repellent need to be reapplied, ensure a safe distance away from the sampling locations and equipment (i.e., more than 10 meters (m) away). Wash hands after application and don new gloves following hand washing.

6.4 Visitors

Visitors to the site are asked to remain at least 10 m from sampling areas.

7 Health and Safety Considerations

7.1 Biological and Environmental Hazard Controls

7.1.1 Sunscreens and Insect Repellents

When site conditions warrant, insect repellent and sunscreen should be applied. Some insect repellents and sunscreen have been approved for PFAS sampling by individual states. According to Michigan Department of Environmental Quality (MDEQ; now known as Michigan Department of Environment, Great Lakes, and Energy [EGLE]), the products below are allowable (MDEQ 2018). Note that California State Water Quality Control Board's PFAS sampling guidance refers to MDEQ/EGLE's allowable list of sunscreens and insect repellents (California State Water Quality Control Board 2020).

Insect Repellents

- OFF Deep Woods
- Sawyer Permethrin

Sunscreen

- Banana Boat Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Meijer Sunscreen Lotion Broad Spectrum SPF 30
- Neutrogena Ultra-Sheer Dry-Touch Sunscreen Broad Spectrum SPF 30
- Banana Boat for Men Triple Defense Continuous Spray Sunscreen SPF 30
- Banana Boat Sport Performance Coolzone Broad Spectrum SPF 30
- Banana Boat Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Banana Boat Sport Performance Sunscreen Stick SPF 50
- Coppertone Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50
- Coppertone Sport High-Performance AccuSpray Sunscreen SPF 30
- Coppertone Sunscreen Stick Kids SPF 55
- L'Oréal Silky Sheer Face Lotion 50+
- Meijer Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50
- Meijer Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70
- Neutrogena Beach Defense Water + Sun Barrier Lotion SPF 70
- Neutrogena Beach Defense Water + Sun Barrier Spray Broad Spectrum SPF 30
- Neutrogena Pure & Free Baby Sunscreen Broad Spectrum SPF 60+

Please plan for sampling events and purchase these products ahead of time. For any sunscreens and bug sprays, including those listed above, always follow these instructions for application:

- Insect repellents and sunscreen should be applied away from the work area prior to initiating sampling.
- When re-applying, stay at least 10 m away from the sampling locations and equipment.
- Wash hands after application and don new nitrile gloves.

7.1.2 Rain Event

Special care should be taken when rain is falling at the project site:

- Field sampling during extreme rainfall should be avoided if possible. If sampling needs to take place during a rain event (or other extreme weather condition), ensure the rain gear or other safety clothing is appropriate. For example, rain gear made from the following materials is allowable: polyurethane, PVC, wax coated fabrics, rubber/neoprene, uncoated Tyvek® (MDEQ 2018).
- If project timelines are tight, consider the use of a gazebo tent that can be erected over the top of the monitoring well to provide shelter from the rain. The canopy material is possibly a PFAS-treated surface and should be managed as such; therefore, wear gloves when moving the tent, change them immediately after moving the tent, and avoid further contact with the tent until all sampling activities have been finished and the team is ready to move on to the next site.

7.1.3 Other H&S Considerations

- ***If an unapproved or potentially suspect hazard control is needed for health and safety, apply or keep that control away from the samples, document its use in field notes, and, if it does contact a sample, take an equipment blank with that material.***
- The ability to safely access the surface water sampling locations must be verified before sampling.
- Field activities must be performed in accordance with the site HASP, a copy of which will be present onsite during such activities.
- Safety hazards associated with sampling surface water include fast-moving water, deep water, and steep slopes close to sampling sites. Use extreme caution when approaching sampling sites.
- If thunder or lighting is present, discontinue sampling and take cover until 30 minutes have passed after the last occurrence of thunder or lighting.
- Use caution when removing well caps as well may be under pressure, cap can dislodge forcefully and cause injury.
- Avoid the use of anti-fog sprays on glasses, which may contain PFAS. It's recommended to instead purchase pre-treated anti-fog safety glasses.

8 Procedure

8.1 Field Equipment Cleaning

Reusable field sampling equipment will require cleaning before initial use and between uses. For groundwater sampling, between uses, decontaminate the flow-through cell and any non-dedicated equipment (i.e., interface probe of depth to water meter) that comes into contact with well water. Trowels and other materials used to sample soil samples will also require decontamination, although dedicated, single use equipment such as liners should be used where possible.

After donning a new pair of nitrile gloves:

- Rinse sampling equipment with Alconox or Liquinox® cleaning solution; Scrub equipment with a plastic brush if needed;
- Rinse two times with distilled water or deionized water;
- Rinse one time with “PFAS-free” water or once with methanol/isopropanol/acetone, if it is available, and once with “PFAS-free” water; organic solvents are especially useful for decontaminating soil sampling equipment. If organic cleaning solvents cannot be brought to site, scrub equipment a second time after a single distilled or deionized water rinse, then rinse two times with distilled or deionized water and once with “PFAS-free” water (i.e., two scrubbings and four water rinsings total).
- Collect all rinsate in a sealed pail for disposal. Do not reuse decontamination solutions between sampling locations.

8.2 Borehole/Monitoring Well Development

If a drill rig is being used to drill for soil cores or to install monitoring wells, wear clean nitrile gloves before collecting each continuous soil sample. Additional requirements include the following:

- Verify in writing with the manufacturer that single-use liners used to collect each sample are made of a material that does not contain PFAS;
- Collect soil samples in laboratory-supplied HDPE bottles.
- Store the sample bottles in coolers and keep at a temperature of 0 to 6ºC until transported to the laboratory.

8.2.1 Well Condition Survey/ Water Level Monitoring

Using equipment that has been thoroughly decontaminated according to the procedures in Section 7.1, conduct the well condition surveys and water level monitoring:

- Conduct monitoring well inspections and record water levels.
- Use an interface probe to evaluate presence/absence of non-aqueous phase liquid (NAPL).
- Measure the depth to water from the top of the polyvinyl chloride (PVC) riser and the total depth of the well.
- Record information in the field notes.

8.2.2 Monitoring Well Development and Purging

Follow these requirements for monitoring well development and purging:

- Do not use Teflon™ tubing for purging or sample collection. HDPE tubing is acceptable.
- Do not re-use materials between wells. Upon completion of use, remove all disposable materials (such as HDPE and/or silicone tubing) and place in heavy duty garbage bags for disposal.
- During development of the well, create sufficient energy to agitate the water column and create flow reversals in the well screen, filter pack and formation to loosen fine-grained materials and draw them into the well. The pumping or bailing action should then draw all drilling fluids and fine-grained material out of the borehole and adjacent formation and then out of the well. Review the Arcadis Monitoring Well Development guidance (Arcadis 2010) for more detailed information.
- Follow the low-flow purge and sampling techniques per the U.S. Protection Agency's (EPA's) guidance document titled *Low Stress (Low Flow) purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells* (2010) and ASTM's standard titled *Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations* (2002). Also available for review is the Arcadis Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells (Arcadis 2011).
- To purge the well, if using HDPE tubing and a peristaltic pump, insert the end of the tubing to the approximate depth of the midpoint of the screened section of the monitoring wells. Measure the length of HDPE tubing to be inserted into each monitoring well and pre-cut it to approximate lengths (such as the previously measured arm span of a field technician) to avoid contact with any materials other than the monitoring well and peristaltic pump. Flow rates should be as low as can be reasonably achieved. Collect and appropriately dispose of purge water.
- Silicone tubing should direct the purge water through a flow-through cell for field parameter measurements of pH, conductivity, temperature, dissolved oxygen, and turbidity. Calibrate the instrument in the field prior to use. Decontaminate the instrument and flow-through cell at each monitoring well location before purging.
- Record field parameters in intervals (generally of 3-minute duration) to ensure purge water has cycled through the flow-through cell. Sample the wells after field parameter measurements indicate stabilization, which allows collection of representative formation water (generally acceptable standards are three consecutive pH readings to within ±0.1 units, and three consecutive conductivity, temperature and dissolved oxygen measurements to within 3%). Turbidity must be monitored, but does not need to be used as a stabilization indicator of purge completion. Record field parameter measurements at each well. Drawdown should be monitored throughout the purge.
- If wells are suspected to be dewatering throughout the purge (i.e., reduced flow rate/difficulty pumping water or bubbles begin to come through the flow through cell), turn off the pump and allow the water level to recover for ½ hour, followed by sample collection. Document these activities in the field notes.

8.3 Sample Collection

Different laboratories may supply sample collection bottles of varying sizes depending on the type of media to be sampled.

8.3.1 Sample Containers

- Collect samples in HDPE bottles fitted with a HDPE lined (no Teflon™) screw cap.
- Complete bottle labels after the caps have been placed back on each bottle.
- Do not use glass bottles due to potential loss of analyte through adsorption. This is particularly important for aqueous samples.
- Review with analytical lab the sample size, sample container, etc. depending upon the type of PFAS analysis that is being requested.

8.3.2 Soil Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Trowels or drilling equipment that will come into contact with a sample should be decontaminated prior to sample collection, preferably with methanol/isopropanol/acetone;
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.

During Sample Collection

- Collect soil samples using a clean stainless-steel trowel or with single-use PFAS-free liners;
- Place soil samples in labeled HDPE bottles supplied by the laboratory.
- Note the time on the sample label.
- Collect any necessary duplicates/co-located samples and matrix spikes – verify with laboratory whether they need to be collected in separate sample bottles.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes.
- Place soil sample bottles in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. Do not use blue ice.

8.3.3 Groundwater Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the labeled HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.
- Measure depth to water and field parameters. Turbidity and the physical appearance of the purged water should be noted on the Groundwater Sampling Log.

During Sample Collection

- Start groundwater sample collection upon stabilization of field parameters.
- If low-flow groundwater sampling techniques are being used, disconnect the silicone tubing from the flow-through cell, enabling collection of groundwater samples without passing through the cell.
- Hydrasleeves are also considered acceptable for sampling of PFAS in groundwater – consult the project manager to determine which technique should be used. In general, low flow sampling is preferable.
- Collect groundwater samples (to the neck of the bottle, some headspace is acceptable) from the dedicated sampling ports at the center of the well screen. While collecting the sample, make sure the bottle cap remains in the other hand of the sampler, until replaced on the bottle.
- To mitigate cross contamination, collect groundwater samples in a pre-determined order from least impacted to greater impacted based on previous analytical data or knowledge about past activities at the site. If no analytical data are available, samples are to be collected in the following order:
    1. First sample the upgradient well(s).
    2. Next, sample the well located furthest downgradient of the interpreted or known source.
    3. The remaining wells should be progressively sampled in order from downgradient to upgradient, such that the wells closest to the interpreted or known source are sampled last.
- NOTE: If high concentrations of PFAS related to class B firefighting foams are expected in a groundwater sample, conduct a Shaker test by collecting and shaking a small portion of the sample (~10 to 25 mL) on site in a small disposable vial. If foaming is noted within the sample, document the foaming when samples are

submitted for analysis; the 'shaker test' vial can then be disposed. This shaker test provides information about how each of the samples should be handled analytically.

- After collecting the sample, tightly screw on the polypropylene cap (snug, but not too tight). This will minimize leaking or cross contamination of the sample. Most PFAS, including all analytes measured by USEPA Method 537, are not volatile at environmental pH.
- Note the time on the sample label.
- Collect any necessary duplicates and matrix spikes. As the laboratory should be analyzing the entire aqueous sample rather than sub-sampling, separate bottles will be required for these samples.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.
- Do not rinse PFAS sample bottles during sampling. Do not filter samples.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes and COC. Note ‘shake test’ results if appropriate.
- Place groundwater samples in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**

  Treat all disposable sampling materials as single use and dispose of them appropriately after sampling at each monitoring well.

8.3.4 Sediment Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.

During Sample Collection

- Where surface water samples and sediment samples are collected at the same location, collect surface water samples first to minimize siltation.

- Collect sediment samples either manually using a stainless-steel trowel or using a petite ponar grab sampler, depending on field conditions at each sampling location during sampling program.
- Collect sediment samples from the upper 10 cm of sediment.
- For a sample to be acceptable overlying, low turbidity water must be present.
- Decant the overlying water and use a stainless-steel trowel to collect only the upper 5 centimeters (cm) of sediment.
- Collect sediment samples directly into laboratory-supplied bottles that are suitable in both material and size.
- Do not overfill the sample bottle.
- Make sure that the sample does not contain vegetation, that the sediment is undisturbed, and that the sampler shows no signs of winnowing or leaking.
- Make sure bottle caps remain in the gloved hand of the sampler until sampling is complete and caps are replaced on the bottle.
- Note the time on the sample label.
- Collect any necessary duplicates and matrix spikes.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes.
- Place samples in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**
- Measure surface water pH, conductivity, temperature, and total dissolved solids (TDS) at each location **after** both surface water and sediment sampling is completed.

8.3.5 Surface Water Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.

- Use the HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.

During Sample Collection

- Avoid sampling the surface, in general.
- However, for Air Force investigations, collect samples from the water surface.
- Where surface water samples and sediment samples are collected at the same location, collect surface water samples first to minimize siltation.
- Collect surface water samples directly into laboratory-supplied bottles; wide-mouth bottles may be preferable to narrow mouth bottles for ease of surface water collection.
- Make sure bottle caps remain in the gloved hand of the sampler until sampling is complete and caps are replaced on the bottle.
- Note the time on the sample bottle.
- Collect any necessary duplicates and matrix spikes. As the laboratory should be analyzing the entire aqueous sample rather than sub-sampling, separate bottles will be required for these samples.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes.
- Place samples in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**
- Measure surface water pH, conductivity, temperature, and TDS at each location **after** both surface water and sediment sampling.

8.4 Shipping

- If samples cannot be shipped the same day as collected, arrange an appropriate means of keeping the samples cool overnight and maintain the temperature between 0 and 10°C for the first 48 hours after collection, and then between 0 and 6°C thereafter.
- Store samples in appropriate transport bottles (coolers) with ice (Ziploc© bags for use as ice containers) with appropriate labeling. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**

- Complete the appropriate procedures for COC, handling, packing, and shipping.
- Fill out and check COC Forms against the labels on the sample bottles progressively after each sample is collected.
- Place all disposable sampling materials (such as plastic sheeting, and health and safety equipment) in appropriate containers.
- Ship samples via courier service with priority overnight delivery. Tracking numbers for all shipments should be provided and recorded after they have been sent out to ensure their timely delivery.
- Do not ship samples via Fed Ex for Saturday delivery.

9 Waste Management

All rinsate should be collected in a sealed pail for disposal. Drill cuttings and purge water will be managed as specified in the Field Sampling Plan (FSP) or Work Plan, and according to state and/or federal requirements. PPE and decontaminated fluids will be contained separately and staged at the sampling location. Containers must be labeled at the time of collection. Labels will include date, location(s), site name, city, state, and description of matrix contained (e.g., soil, groundwater, PPE). General guidelines for investigation derived waste (IDW) handling and storage are set forth in a separate IDW guidance document (Arcadis 2009).

Typical waste characterization procedures include collection of a composite sample of the drill cutting material and a composite sample of the purge water for laboratory analysis. Samples are typically analyzed for disposal toxicity characteristic leaching procedure (TCLP) analysis for metals and VOCs. For PFAS, a simple leach test with neutral pH water may be more indicative of actual risk. Additionally, generators of waste are required to include analysis of other constituents that are reasonably believed to be present including (in this case) PFAS.

Waste storage and final waste disposition should be determined in the site specific workplan.

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

If digital data collection isn't possible, waterproof field books should be avoided for field notes. Instead, field notes on loose paper on Masonite, plastic, or aluminum clip boards is preferred. Please note that newer Rite in the Rain® notebooks are approved for PFAS sampling. Other requirements for field notes include:

- Pens, pencils, and fine/ultra-fine point Sharpies® may be used.
- Keep field notes and writing implements away from samples and sampling materials.
- One person should conduct sampling while another records field notes.

- Do not write on sampling bottles unless they are closed.

10.1 Other Project Documentation

- Complete groundwater and/or soil sampling logs.
- Make sure COC Forms are properly completed. Verify which PFAS analytes (e.g., just PFOS and PFOA, some or all of the 537 list, etc.) are required for analysis and note on the COC.

11 Quality Assurance

Refer to quality control requirements for the project to ensure that appropriate quality assurance and quality control (QA/QC) samples are collected. When collecting QA/QC samples, the same guidelines apply as when collecting regular samples – specifically that:

- Samples should be collected in laboratory-supplied HDPE bottles;
- Bottle caps must remain in the hand of the sampler until replaced on the bottle;
- Labels must be completed after the caps have been placed back on each bottle; and
- Samples must be stored in appropriate transport bottles (coolers) with ice (Ziploc© bags for use as ice containers) with appropriate labeling. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**

11.1 Equipment Blanks (if relevant)

QA/QC sampling typically includes daily collection of equipment blanks using the laboratory-supplied “PFAS-free” water. For peristaltic pump tubing, laboratory supplied “PFAS-free” water should be poured into a clean HDPE sample bottle and then pumped through new HDPE tubing using the peristaltic pump (with new silicone tubing). The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated. Note that an equipment blank can also be collected if an unapproved or potentially suspect hazard control is needed for health and safety and it contacts a sample, i.e., that material would be exposed to PFAS free water then the water would be collected in a separate sample container.

11.2 Field Duplicates

QA/QC sampling typically includes the collection of one field duplicate for every 10 or 20 samples collected. Each duplicate sample will be collected immediately after the initial sample of which it is a duplicate into a separate laboratory-provided sample bottle. Do not indicate to the laboratory which sample the duplicate replicates, i.e., it should be given a blind reference on the COC and sample name such as “duplicate”.

11.3 Field Reagent Blanks

QA/QC sampling for PFAS typically includes the submission of one laboratory supplied field reagent blank per day. The field reagent blank sample is brought to the site in a laboratory-supplied sample bottle. Field staff

transfer the laboratory-supplied reagent blank to an empty sample bottle. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel and should be placed in the same cooler as the other PFAS samples.

11.4 Matrix Spikes (optional in some cases)

QA/QC sampling includes submitting a sample to be used as a matrix spike if the project requires it. If a separate sample bottle is required, an additional sample will be collected immediately after the initial sample of which it is a duplicate into a separate laboratory-supplied sample bottle.

11.5 Laboratory Analytical QA/QC

- Arcadis recommends that any request for PFAS analysis in groundwater or soil should be conducted by an ELAP-accredited method compliant with QSM 5.3 Table B-15. Requirements laid out in Table B-15 strictly govern acceptable laboratory data quality for PFAS analysis in environmental samples. **For all data collection efforts at DoD sites, PFAS data must be obtained using a method that is DoD ELAP-accredited under QSM 5.3 or later.**
- Laboratory QA/QC should consist of one laboratory blank and one laboratory control sample (or blank spike) per batch of samples, and additional QA/QCs as indicated by the laboratory QA/QC procedures.
- Isotope dilution should be used for quantification with isotope-labeled surrogate standards, as available, according to the guidelines of QSM 5.3 Table B-15. The USEPA has two drinking water methods (USEPA Method 537.1 and USEPA Method 533). Method 537.1 does not allow for isotope dilution but USEPA Method 533 requires isotope dilution.
- For drinking water, groundwater, and surface water samples, laboratories must extract the entire sample and include a solvent rinse of the bottle for analysis. Aqueous samples should generally not be sub-sampled prior to analysis, unless they are high concentration and require serial dilution (US DoD 2017).
- Soil samples should be analyzed in their entirety or thoroughly homogenized before extraction and analysis.
- As part of the internal QA/QC of laboratory results, relative percent difference (RPD) should be calculated between samples and corresponding field or laboratory duplicates. The laboratory quality assurance portion of the laboratory certificates should be reviewed to verify that all calculations/recoveries were within acceptable limits as established by the laboratory method and guidelines in Table B-15 of QSM 5.3 or later (USDoD 2019).

12 References

Arcadis Australia. 2017. Soil and Concrete Sampling for PFAS. April.

Arcadis. 2010. Monitoring Well Development, Rev. #2.2. March 22.

Arcadis. 2009. Investigation-Derived Waste Handling and Storage, Rev. #2. March 6.

Arcadis. 2011. Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells, Rev. #4. February 2.

ASTM. 2002. ASTM D6771-02 - Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations (Withdrawn 2011). Available at: https://www.astm.org/Standards/D6771.htm.

California State Water Quality Control Board. 2020. Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines for Non-Drinking Water. September. https://www.waterboards.ca.gov/pfas/docs/sept_2020_pfas_sampling_guidelines.pdf

Department of Environment Regulation (DER). Government of Western Australia. 2016. Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS). Contaminated Sites Guidelines. February.

Michigan Department of Environmental Quality (MDEQ). 2018. General PFAS Sampling Guidance. October. https://www.michigan.gov/documents/pfasresponse/General_PFAS_Sampling_Guidance_634597_7.pdf

Massachusetts Department of Environmental Protection (MassDEP). 2017. DRAFT Fact Sheet, Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the Massachusetts Contingency Plan. January.

New Hampshire Department of Environmental Services (NHDES). 2016. Perfluorinated Compound (PFC) Sample Collection Guidance. November.

United Nations Environment Programme (UNEP). 2015. PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convention, Set-up and guidelines for monitoring. Jana Weiss, Jacob de Boer, Urs Berger, Derek Muir, Ting Ruan, Alejandra Torre, Foppe Smedes, Branislav Vrana, Fabrice Clavient, and Heidelore Fiedler. Division of Technology, Industry and Economics. Geneva. April.

United States Army Corps of Engineers (USACE). 2016. DRAFT – Standard Operating Procedure 047: Per/Poly Fluorinated Alkyl Substances (PFAS) Field Sampling. Revision: 1. March.

U.S. Army Corps of Engineers – Omaha District. 2016. Chemistry Requirements – PFAS.

U.S. Department of Defense (DoD). 2019. Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.3. In conjunction with the U.S. Department of Energy. May.

U.S. Environmental Protection Agency. 2009. USEPA Method 537: Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), version 1.1, September. National Exposure Research Laboratory, Office of Research and Development.

U.S. Environmental Protection Agency. 2010. Low Stress (Low Flow) purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells. Available at: https://www.epa.gov/quality/low-stress-low-flow-purging-and-sampling-procedure-collection-groundwater-samples-monitoring.

Transport Canada. February 2016, Per-and Polyfluorinated Alkyl Substances (PFAS) Field Sampling Guidance.

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Attachment 2

Standard Field Forms

Daily Log

Project Name : RACER Pontiac North Campus 2023 **Weather(°F) :**
Project Number : **Prepared By:**
Purpose :
PPE :
Equipment:

Date	Time	Description of Activities

Signature:

Waste Management:

Drums On Site

Date	Are there any waste drums on site?	Number of Drums upon Arrival	Size of Drums	Type of Drums	Condition of Drums	Waste Drummed Today?	Number of drums Created	Size of drums	Condition of Drums	General Waste Comments

Other Photos

Equipment and Calibration Information:

Supplier: **Model:**
Rental Number: **Calibrated:**
Bump Checked: **Calibration Passed:**

Water Quality Meter SN:

Date	Time	Calibrated Fluid and Value	Lot #	Expiration Date	Initial Reading	Final Reading

Calibration Documents

Equipment and Calibration Information:

Supplier: **Model:**
Rental Number: **Calibrated:**
Bump Checked: **Calibration Passed:**

Turbidity Meter SN:

Date	Time	Calibrated Fluid and Value	Lot #	Expiration Date	Reading

Groundwater Sampling Form

Project Number		**Well ID**		**Date**
Project Name/Location	RACER Pontiac North Campus 2023	**Weather(°F)**		
Measuring Pt. Description		**MP Elevation**	**Casing Diameter (in)**	**Well Casing Material**
Static Water Level (ft-bmp)		**Total Depth (ft-bmp)**	**Water Column (ft)**	**Gallons in Well**
Purge Start		**Pump Intake (ft-bmp)**	**Purge Method**	**Purge Equipment**
Purge End		**Volumes Purged**	**Sample ID**	**Sampled by**
Sample Time		**Gallons Purged**	**Replicate/ Code No.**	**Sample Type**

Time	Minutes Elapsed	Total Elapsed Minutes	Rate mL/min	Depth to Water (ft)	Gallon Purged	pH (standard units)	Conductivity (mS/cm)	Turbidity (NTU)	Dissolved Oxygen (mg/L)	Temperature °C	Redox (mV)	Appearance	
												Color	Odor

Comments:

Well Casing Volume Conversion

Well diameter (inches) = gallons per foot — 1 = 0.04; 1.5 = 0.09; 2.5 = 0.26; 3.5 = 0.50; 6 = 1.47
1.25 = 0.06; 2 = 0.16; 3 = 0.37; 4 = 0.65

Well Information

Well Location: _____ Well Locked at Arrival: _____

Condition of Well: _____ Well Locked at Departure: _____

Well Completion: _____ Key Number To Well: _____

_____

ft-bmp = feet below measuring point
in = inches
ft = feet
mL/min = milliliters per minute
mS/cm = milliSiemens per centimeter
NTU = Nephelometric Turbidity Unit
mg/L = milligrams per liter
mV = milliv

CHAIN-OF-CUSTODY Analytical Request Document

Pace Analytical

Submitting a sample via this chain of custody constitutes acknowledgment and acceptance of the Pace Terms and Conditions found at: https://info.pacelabs.com/hubfs/pas-standard-terms.pdf

Chain-of-Custody is a LEGAL DOCUMENT - Complete all relevant fields

LAB USE ONLY- Affix Workorder/Login Label Here or List Pace Workorder Number or MTJL Log-in Number Here

ALL BOLD OUTLINED AREAS are for LAB USE ONLY

Company:	Billing Information:
Address:	
Report To:	Email To:
Copy To:	Site Collection Info/Address:
Customer Project Name/Number:	State: County/City: Time Zone Collected: / [ ]PT [ ]MT [ ]CT [ ]ET

Phone: Email:	Site/Facility ID #:	Compliance Monitoring? [ ] Yes [ ] No
Collected By (print):	Purchase Order # : Quote #:	DW PWS ID #: DW Location Code:
Collected By (signature):	Turnaround Date Required:	Immediately Packed on Ice: [ ] Yes [ ] No
Sample Disposal: [ ] Dispose as appropriate [ ] Return [ ] Archive: _____ [ ] Hold: _____	Rush: (Expedite Charges Apply) [ ] Same Day [ ] Next Day [ ] 2 Day [ ] 3 Day [ ] 4 Day [ ] 5 Day	Field Filtered (if applicable): [ ] Yes [ ] No Analysis: _____

* Matrix Codes (Insert in Matrix box below): Drinking Water (DW), Ground Water (GW), Wastewater (WW), Product (P), Soil/Solid (SL), Oil (OL), Wipe (WP), Air (AR), Tissue (TS), Bioassay (B), Vapor (V), Other (OT)

Customer Sample ID	Matrix *	Comp / Grab	Collected (or Composite Start) Date	Collected (or Composite Start) Time	Composite End Date	Composite End Time	Res Cl	# of Ctns	Container Type: Plastic (P) or Glass (G)

Container Preservative Type **

Analyses

** Preservative Types: (1) nitric acid, (2) sulfuric acid, (3) hydrochloric acid, (4) sodium hydroxide, (5) zinc acetate, (6) methanol, (7) sodium bisulfate, (8) sodium thiosulfate, (9) hexane, (A) ascorbic acid, (B) ammonium sulfate, (C) ammonium hydroxide, (D) TSP, (U) Unpreserved, (O) Other _____

Lab Project Manager:

Lab Profile/Line:

Lab Sample Receipt Checklist:

Custody Seals Present/Intact	Y	N	NA
Custody Signatures Present	Y	N	NA
Collector Signature Present	Y	N	NA
Bottles Intact	Y	N	NA
Correct Bottles	Y	N	NA
Sufficient Volume	Y	N	NA
Samples Received on Ice	Y	N	NA
VOA - Headspace Acceptable	Y	N	NA
USDA Regulated Soils	Y	N	NA
Samples in Holding Time	Y	N	NA
Residual Chlorine Present	Y	N	NA

Cl Strips: _____

Sample pH Acceptable Y N NA

pH Strips: _____

Sulfide Present Y N NA

Lead Acetate Strips: _____

LAB USE ONLY:

Lab Sample # / Comments:

Customer Remarks / Special Conditions / Possible Hazards:

Type of Ice Used: Wet Blue Dry None

Packing Material Used:

Radchem sample(s) screened (<500 cpm): Y N NA

SHORT HOLDS PRESENT (<72 hours) : Y N N/A

Lab Tracking #:

Samples received via: FEDEX UPS Client Courier Pace Courier

LAB Sample Temperature Info:

Temp Blank Received: Y N NA

Therm ID#: _____

Cooler 1 Temp Upon Receipt: __oC

Cooler 1 Therm Corr. Factor: ___oC

Cooler 1 Corrected Temp: _____oC

Comments:

Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:

MTJL LAB USE ONLY

Table #:

Acctnum:

Template:

Prelogin:

PM:

PB:

Trip Blank Received: Y N NA

HCL MeOH TSP Other

Non Conformance(s): YES / NO

Page: _____ of: _____

Attachment 3

Equipment Manufacturer Calibration Procedures

Conductivity

The conductivity calibration should be verified every day the instrument is used. However, the conductivity sensor is very stable and may hold its calibration for several weeks.

CALIBRATION TIPS

1. It is not necessary to calibrate conductivity, specific conductance and salinity. Calibrating one of these parameters will simultaneously calibrate the others. YSI recommends calibrating specific conductance (temperature compensated conductivity) for greatest ease and accuracy.
2. Ensure the conductivity sensor is clean and dry before performing a specific conductance calibration.
3. Always use fresh, traceable conductivity calibration solution when calibrating the conductivity sensor.
    a. The shelf life of conductivity solution is one month after being opened. This is due to potential changes in the value of the solution caused by evaporation which can occur after opening the bottle. Be sure to write the open date on the bottle so you know that you are using good calibration solution.
    b. Never calibrate with a conductivity solution that is less than 1.0 mS/cm. You are setting the slope on a linear device so a good strong conductivity signal will give you the best performance. Use 1.0 mS/cm for fresh water, 10 mS/cm for brackish to estuarine water and 50 mS/cm for salt water. 1.0 mS (millisiemens) = 1000 uS (microsiemens).
4. Pre-rinse the cal cup and sensors with a small amount of calibration standard or rinse standard and discard.
5. When calibrating the conductivity sensor, the calibration solution must cover the top vent holes of the conductivity sensor. If using a Quatro cable, the top vent hole is located on the side of the combination conductivity/temperature sensor. If using a different cable, the conductivity sensor is integral to the cable and the sensor has two vent holes located close to the cable. Ensure the entire conductivity sensor is submerged in the solution or the instrument will read approximately half the expected value.
6. After placing the sensor into the solution, gently move the sensor up and down to remove any air bubbles that may be trapped in the conductivity sensor.
7. If calibrating Specific Conductance, enter the value of the conductivity solution as it is listed for 25°C. Make sure you are entering the correct units. 1 mS = 1,000 uS.
8. If you receive a warning message stating that the calibration is questionable, do <u>not</u> continue with the calibration. Instead, select 'No' and investigate what is causing the questionable results. If you accept a questionable calibration, your conductivity readings (and your DO mg/L readings) will be erroneous. Typical causes for this error message include: incorrect entries (entering 1000 uS/cm instead of 1.0 mS/cm), not using enough solution to cover the vent holes, air bubbles trapped in the sensor, calibrating in conductivity instead of specific conductance, dirty conductivity electrodes, and/or bad calibration solution.
9. After accepting a good calibration, navigate to the GLP file and check the conductivity cell constant for the calibration. For highest accuracy, the cell constant should be 5.0 +/- 0.5. However, the acceptable range is 5 +/- 1.0. A cell constant outside of this range indicates that a questionable calibration was accepted.

TROUBLESHOOTING TIPS

If you get an error message during calibration, be sure that you are:

1. Entering the correct calibration value (1 mS/cm = 1000 uS/cm).
2. Calibrating in Specific Conductance mode.
3. Using enough solution to cover the vent holes on the sensor.
4. Dislodging any air bubbles that could be trapped in the sensor.
5. Using a fresh, traceable conductivity calibration solution.

If you are following the above recommendations and still receiving an error message, check the conductivity sensor to make sure it is clean. A clean conductivity sensor should read less than 3 uS/cm in dry air. If your sensor is dry and giving you a reading higher than 3 uS/cm in air, it should be cleaned.

The conductivity calibration generates its cell constant value after calibration. The ideal cell constant is 5.0 +/-0.5 but 5.0 +/- 1.0 is acceptable. Any significant jump or change in this number from one calibration to the next usually indicates a problem with the calibration and/or sensor. If you are sure that your calibration standard is good and your calibration process is correct, then your sensor may need to be cleaned.

Cleaning the Conductivity Sensor

The openings that allow sample access to the conductivity electrodes should be cleaned regularly. The small cleaning brush included in the Maintenance Kit is intended for this purpose. Dip the brush in clean water and insert it into each hole 10 to 12 times. In the event that deposits have formed on the electrodes, it may be necessary to use a mild detergent (laboratory grade soap or bathroom foaming tile cleaner) with the brush. Rinse thoroughly with clean water, then check the response and accuracy of the conductivity sensor with calibration solution.

Quatro Cables

Quatro cables have a replaceable combination conductivity/temperature sensor (p/n 5560). All other Pro Plus cables have integral conductivity sensors. If using a Quatro cable and your conductivity sensor is not calibrating or is reading > 3 uS/cm in dry air after being cleaned, remove the conductivity/temperature sensor from the cable. The Pro Plus should read < 3 uS/cm for conductivity (not specific conductance) without a conductivity sensor installed. If the instrument is reading > 3 uS/cm without a sensor installed, the conductivity/temperature port on the cable may be contaminated. Refer to the Cleaning the Sensor Port section of this document for information on how to clean the port.

If the conductivity measurement continues to read more than 3 uS/cm without a conductivity/temperature sensor installed, there may be a problem with the cable and/or instrument. In this case, contact your local YSI Representative or a YSI Authorized Service Center.

Other Pro Plus Cables

If your conductivity sensor is not calibrating or is reading > 3 uS/cm in dry air after performing a sensor cleaning, contact your local YSI Representative or a YSI Authorized Service Center.

pH

The pH calibration should be verified every day the instrument is used. However, a new pH sensor may be capable of holding its calibration for several days.

CALIBRATION TIPS

1. If using a pH sensor in a 6051010 or Quatro cable, calibrate the sensor in port 1 prior to calibrating the sensor in port 2. The sensor in port 2 uses the reference of the sensor installed in port 1. Therefore, it is important to verify that the port 1 sensor is working properly before calibrating the port 2 sensor. See pH Troubleshooting Tips for additional info.
2. The pH sensor can be calibrated with up to six calibration points.
3. Calibration can be accomplished in any buffer order.
4. pH 7 buffer should be used regardless of how many calibration points you use; however, it does not have to be the first point.
5. In most cases, a two-point calibration is all that is required (4 and 7 or 7 and 10). You can bracket the expected in-situ pH values. Use a three-point calibration with 4, 7 and 10 if the in-situ pH values are unknown or if you expect the in-situ values to be on both sides of the pH scale.
6. Rinse the sensors and cal cup with a small amount of pH buffer. Fill the cup so that the pH sensor tip and the temperature sensor are submerged in buffer.
7. If necessary, highlight the Calibration Value and enter the pH value of the buffer solution. Note: The Pro Plus has auto buffer recognition which can be set to USA (4, 7, 10) or NIST (4.01, 6.86, 9.18) buffer values in the pH Sensor Setup menu.
8. Record the pH millivolts for each calibration point. The acceptable mV outputs for each buffer are shown below.

   pH 7 mV value = 0 mV +/- 50 mV
   pH 4 mV value = +165 to +180 from 7 buffer mV value
   pH 10 mV value = -165 to -180 from 7 buffer mV value

   - A value of +50 or -50 mVs in buffer 7 does not indicate a bad sensor.
   - The mV span between pH 4 and 7 and 7 and 10 mV values should be ≈ 165 to 180 mV. 177 is the ideal distance. The slope can be 55 to 60 mV per pH unit with an ideal of 59 mV per pH unit.
   - If the mV span between pH 4 and 7 or 7 and 10 drops below 160, clean the sensor and try to recalibrate.
9. Wait for the pH to stabilize in the each buffer and then press enter to accept each calibration point.
10. Rinse the sensor and cal cup with a small amount of the next buffer between calibration points.
11. After pressing enter to accept your last calibration point, press cal (Cal) to complete the calibration. Otherwise you will continue calibrating up to 6 calibration points.
12. If you receive a warning message stating that the calibration is questionable, do not continue with the calibration. Instead, select 'No' and investigate what is causing the questionable results. If you accept a questionable calibration, your pH readings will be erroneous. Typical causes for this error message include: incorrect Sensor/Port setup in the instrument, a dirty sensor or bad buffer solution.
13. After accepting a good calibration, navigate to the GLP file and check the pH Slope and Slope % of ideal. A good slope should be between 55 and 60 mVs while the ideal is 59 mV. If the slope drops below 53, the sensor should be reconditioned and recalibrated.

TROUBLESHOOTING TIPS

Typical working life for pH sensors is approximately 12-24 months depending on usage, storage and maintenance. Proper storage and maintenance generally extends the sensor's working life.

Clean and recondition the sensor if a slow response in the field has been reported or if it takes more than 90 seconds to stabilize in pH buffer.

If you get an error message during a pH calibration, check the following:

1. Ensure the pH buffers are good and not expired
2. Ensure that the pH sensor is installed in the correct port of the cable and the correct ISE is enabled in the Sensor Setup menu.
    a. If using a pH or pH/ORP combo sensor in a 6051020 cable, ensure the sensor is installed in port 1.
    b. If using a pH or pH/ORP combo sensor in a 60510, 6051020 or 6051030 cable, pH should be enabled in ISE1 of the instrument's Sensor Setup menu.
    c. If using a pH sensor in a 6051010 or Quatro cable, check to see if the pH sensor is installed in port 1 or port 2. If the pH sensor is installed in port 1, enable pH in ISE1 of the Sensor Setup menu. If the pH sensor is installed in port 2, enable pH in ISE2 of the Sensor Setup menu. Note: It is not recommended to use a pH/ORP combo sensor in 6051010 or Quatro cables. If using a pH/ORP combo sensor in a 6051010 or Quatro cable, ORP will not be measured or reported.
3. If using a 6051010 or Quatro cable, you must have a sensor installed in port 1 for port 2 to operate. Additionally, ensure that the sensor installed in port 1 is in good working order. In 6051010 and Quatro cables, the sensors installed in port 1 and port 2 use the reference from the sensor installed in port 1 only. Therefore, if the sensor installed in port 1 is not working properly, the readings from the sensor installed in port 2 will be erroneous. For greatest ease, install a pH sensor in port 1 of both 6051010 and Quatro cables and your other ISE sensor in port 2.
4. If you continue to get error messages during calibration, clean and recondition the sensor.

Cleaning and Reconditioning the pH, ORP or pH/ORP Sensor

If the pH or pH/ORP sensor has been allowed to dry out or has been stored in distilled or deionized water for an extended period of time, soak the sensor in buffer 4 overnight to try and restore functionality.

Cleaning is required whenever deposits or contaminants appear on the glass and/or platinum surfaces or when the sensor's response slows. The cleaning can be chemical and/or mechanical.

Removing the sensor from the cable may make cleaning easier. Initially, moisten a soft clean cloth, lens cleaning tissue or cotton swab to remove all foreign material from the glass bulb and/or platinum button. Then use a moistened cotton swab to carefully remove any material that may be blocking the reference electrode junction of the sensor. ***CAUTION***: When using a cotton swab, be careful NOT to wedge the swab between the guard and the glass sensor. If necessary, remove cotton from the swab tip, so that the cotton can reach all parts of the sensor tip without stress. You can also use a pipe cleaner for this cleaning if more convenient.

If good pH and/or ORP response is not restored, perform the following additional procedure:

1. Soak the sensor for 10-15 minutes in clean water containing a few drops of commercial dishwashing liquid.
2. GENTLY clean the glass bulb and platinum button by rubbing with a cotton swab soaked in the cleaning solution.
3. Rinse the sensor in clean water, wipe with a cotton swab moistened with clean water, and then re-rinse with clean water.

If good pH and/or ORP response is still not restored, perform the following additional procedure:

1. Soak the sensor for 30-60 minutes in one molar (1 M) hydrochloric acid (HCl). This reagent can be purchased from most lab supply distributors. Be sure to follow the safety instructions included with the acid.

2. Rinse the sensor in clean water, wipe with a cotton swab moistened with clean water (not DI water), and then re-rinse with clean water. To be certain that all traces of the acid are removed from the sensor crevices, soak the sensor in clean tap water for about an hour with occasional stirring.

If biological contamination of the reference junction is suspected or if good response is not restored by the above procedures, perform the following additional cleaning step:

CAUTION: Do not mix the acid from the previous step with the chlorine bleach in the following step. A toxic gaseous product can form from the reaction between the acid and the chlorine bleach. Be certain to copiously rinse the sink and drain system of acid after its disposal and before the disposal of chlorine bleach.

1. Soak the sensor for approximately 1 hour in a 1:1 dilution of commercially available chlorine bleach.
2. Rinse the sensor with clean water and then soak for at least 1 hour in clean tap water with occasional stirring to remove residual bleach from the junction. (If possible, soak the sensor for a period of time longer than 1 hour in order to be certain that all traces of chlorine bleach are removed.) Then re-rinse the sensor with clean water and retest.

Prior to reinstalling the sensor, dry the port and sensor connector with compressed air. If you suspect port contamination, follow the instructions in the Cleaning a Sensor Port section of this document before reinstalling the sensor.

If your pH sensor is still not calibrating after performing a sensor cleaning, contact your local YSI Representative or a YSI Authorized Service Center.

ORP

The ORP calibration should be verified every day the instrument is used. However, a new ORP sensor may be capable of holding its calibration for several days.

CALIBRATION TIPS

1. If using a pH/ORP combination sensor, calibrate pH first to ensure it is working.
2. If using an ORP sensor in a 6051010 or Quatro cable, calibrate the sensor in port 1 prior to calibrating the sensor in port 2. The sensor in port 2 uses the reference of the sensor installed in port 1. Therefore, it is important to verify that the port 1 sensor is working properly before calibrating the port 2 sensor. See ORP Troubleshooting Tips for additional info.
3. Rinse the sensors and cal cup with a small amount of ORP calibration solution. Fill the cup so that the ORP sensor tip and the temperature sensor are submerged in solution.
4. Enter the calibration value per the temperature reading. The value of ORP calibration solution is greatly affected by temperature. The ORP solution should include a chart of solution values per temperature. If not, contact the supplier of the ORP solution to obtain this information. The Pro Series ORP sensors use a Ag/AgCl 3.5 M KCl reference. Be sure the value you enter is for this type of reference. If using the YSI Zobell calibration solution, the Pro Plus will automatically determine the calibration value.
5. Wait for the readings to stabilize and then press enter to accept the calibration.
6. If you receive a warning message stating that the calibration is questionable, do not continue with the calibration. Instead, select 'No' and investigate what is causing the questionable results. If you accept a questionable calibration, your ORP readings will be erroneous. Typical causes for this error message include: incorrect Sensor/Port setup in the instrument, a dirty sensor or bad calibration solution.

TROUBLESHOOTING TIPS

Typical working life for ORP sensors is approximately 12-24 months depending on usage, storage and maintenance. Proper storage and maintenance generally extends the sensor's working life.

Clean and recondition the sensor if the sensor exhibits a slow response in Zobell solution, i.e. it takes more than 90 seconds to stabilize when placed in Zobell.

If you get error messages during an ORP calibration, check the following:

1. Ensure the ORP calibration solution is good and not expired.
2. Ensure that the ORP sensor is installed in the correct port of the cable and the correct ISE is enabled in the Sensor Setup menu.
    a. If using an ORP or pH/ORP combo sensor in a 6051020 cable, ensure the sensor is installed in port 1.
    b. If using an ORP sensor in a 60510, 6051020 or 6051030 cable, ORP should be enabled in ISE1 of the instrument's Sensor Setup menu.
    c. If using a pH/ORP combo sensor in a 60510, 6051020 or 6051030 cable, ORP should be enabled in ISE2 of the instrument's Sensor Setup menu.
    d. If using an ORP sensor in a 6051010 or Quatro cable, check to see if the ORP sensor is installed in port 1 or port 2. If the ORP sensor is installed in port 1, enable ORP in ISE1 of the Sensor Setup menu. If the ORP sensor is installed in port 2, enable ORP in ISE2 of the Sensor Setup menu.
5. If using a pH/ORP combo sensor in a 6051010 or Quatro cable, ORP will not be measured or reported.
6. If using a 6051010 or Quatro cable, you must have a sensor installed in port 1 for port 2 to operate. Additionally, ensure that the sensor installed in port 1 is calibrated and in good working order. In 6051010 and Quatro cables, the sensors installed in port 1 and port 2 use the reference from the sensor installed in

port 1 only. Therefore, if the sensor installed in port 1 is not working properly, the readings from the sensor installed in port 2 will be erroneous.

7. If you continue to get error messages during calibration, clean and recondition the sensor per the instructions in the pH Troubleshooting section of this document. If you suspect port contamination, follow the instructions in the Cleaning a Sensor Port section before reinstalling the sensor.
8. If you continue to have problems, you can check the offset of the ORP sensor by performing a factory reset to the ORP sensor. After resetting the sensor, compare the ORP mV readings in Zobell solution to the calibration value. The difference between values should be less than 100 mVs. If the difference is 80 mVs or higher, consider replacing the sensor as it is nearing the end of its life span.

Dissolved Oxygen

The dissolved oxygen sensor should be calibrated every day the instrument is used. It is not necessary to calibrate in both % and mg/L or ppm. Calibrating in % will simultaneously calibrate mg/L and ppm and vice versa.

CALIBRATION TIPS

1. The Pro Plus can be calibrated in air-saturated water, water-saturated air or against a Winkler Titration. You can perform a 1 or 2 point DO calibration. A 2 point calibration includes 1 point in a zero oxygen environment and the 2nd point at full saturation.
2. For both ease of use and accuracy, YSI recommends that you perform a 1 point calibration in water-saturated air.
3. Make sure that there is a good membrane with fresh electrolyte (O2 probe solution) installed on the DO sensor. The membrane should be clean and free of wrinkles. There should not be any air bubbles present under the membrane. Membranes should be changed regularly and generally last 2-8 weeks depending on use and storage.
4. To perform a 1 point calibration in water-saturated air, place the sensor in a 100% humid environment. This can be accomplished several ways:
    a. For the 60520 and 6052030 cables, moisten the sponge in the gray calibration sleeve with a *small* amount of clean water and place it over the sensor guard.
    b. For the 6051020 and Quatro cables, place a small amount of water in the calibration/storage cup and place it over the sensors. When screwing the calibration cup onto the sensor bulkhead, only engage one or two threads. Do <u>not</u> screw the calibration cup completely onto the sensor bulkhead. The goal is to have air exchange between inside and outside the calibration cup.

    The sponge and calibration sleeve/cup should be clean since bacterial growth may consume oxygen and interfere with the calibration. Be sure the sensor is in air, not water, and that there are not any water droplets on the membrane or temperature sensor.
5. After entering the % calibration mode, wait approximately 5 to 15 minutes for the storage container to become completely saturated and, if using a polarographic sensor, to allow the sensor to stabilize.
6. Salinity affects the ability of water to hold oxygen and is used by the instrument to calculate DO mg/L (ppm). The Salinity value displayed near the top of the DO calibration screen is either the salinity correction value entered in the Sensor menu or the Salinity value as measured by the conductivity sensor in use. If you are using a conductivity sensor, ensure that it is calibrated and reading correctly in order to obtain accurate DO mg/L (ppm) measurements. If you are not using a conductivity sensor, the Salinity correction value should be the salinity of the water you <u>will</u> be testing. Highlight Salinity and press enter to modify this setting if necessary. The salinity of fresh water is typically 0-0.5 ppt and seawater is typically 35 ppt.
7. After accepting the calibration, navigate to the GLP menu and record the DO sensor's value (sensor current in uA). The acceptable sensor currents when calibration is performed at 25°C, in a 100% saturated air environment at 760 mmHg are:

    1.25 mil PE membrane (yellow membrane): Average 6.15 uA (min. 4.31 uA, max. 8.00 uA)
    2.0 mil PE membrane (blue membrane): Average 3.38 uA (min. 2.37 uA, max. 4.40 uA)
    1 mil Teflon membrane: Average 16.29 uA (min. 11.40 uA, max. 21.18 uA)
8. If you receive a warning message stating that the calibration is questionable, do <u>not</u> continue with the calibration. Instead, select 'No' and investigate what is causing the questionable results. If you accept a questionable calibration, your DO readings will be erroneous. Typical causes of a calibration error message include: incorrect sensor, membrane or port setup in the instrument, incorrect barometric pressure information, a bad membrane or a sensor that needs reconditioned.

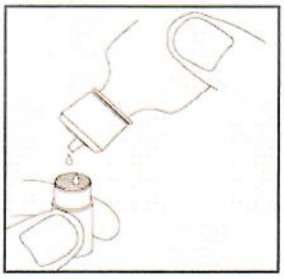
TROUBLESHOOTING TIPS

1. Ensure that the correct sensor type and membrane type are enabled in the Sensor Setup Menu. Galvanic sensors have a gray probe body and Polarographic sensors have a black probe body.
2. If using a 6051020 cable, ensure that the DO sensor is installed in port 2. If using a Quatro cable, ensure that the DO sensor is installed in the port labeled DO.
3. Ensure the Pro Plus barometer is reading accurately. The DO % Saturation calibration uses the instrument's barometric pressure reading for the DO % calibration. If the barometer is not reading accurately, the calibration will be erroneous. The barometer should be reading *true* barometric pressure. If you suspect the barometer reading is incorrect, calibrate the barometer and then recalibrate the DO sensor. Laboratory barometer readings are usually "true" (uncorrected) values of air pressure and can be used "as is" for barometer calibration. Weather service readings are usually not "true", i.e., they are corrected to sea level, and therefore cannot be used until they are "uncorrected". An approximate formula for this "uncorrection" is: True BP in mmHg = Corrected BP in mmHg – [2.5 * (Local Altitude in ft. above sea level/100)]
4. Install a new membrane with fresh electrolyte onto the DO sensor. Ensure you are using the correct electrolyte solution. Polarographic sensors use electrolyte that is in a white labeled bottle (KCl/Na_2SO_4). Galvanic sensors use electrolyte that is in a blue labeled bottle (NaCl).
5. Recondition the DO sensor and then install a new membrane.
6. If you suspect port contamination, remove the sensor and follow the instructions in the Cleaning a Sensor Port section.
7. If you continue to have trouble calibrating the DO sensor, contact your local YSI Representative or a YSI Authorized Service Center.

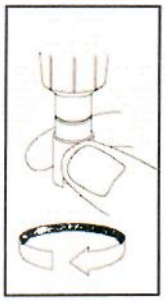
Membrane Cap Installation

The DO membrane and electrolyte solution (O2 solution) should be changed once every 2-8 weeks depending on use and storage. In addition, the membrane and electrolyte solution should be changed if (a) bubbles are visible under the membrane; (b) significant deposits of dried electrolyte are visible on the membrane; or (c) if the sensor shows unstable readings or other sensor-related symptoms. To install a new membrane cap follow these instructions:

1. Remove the sensor guard or cal cup to access the sensor tip.
2. Unscrew and remove any old membrane cap by holding the sensor when unscrewing the membrane cap. Discard the used membrane cap.
3. Thoroughly rinse the sensor tip with distilled or DI water.



4. Fill a new membrane cap with the appropriate electrolyte solution that has been prepared according to the directions on the bottle. Polarographic sensors use electrolyte that is in a white labeled bottle (KCl/Na_2SO_4). Galvanic sensors use electrolyte that is in a blue labeled bottle (NaCl). Be very careful not to touch the membrane surface during this process. Lightly tap the side of the membrane cap to release air bubbles that may be trapped.



5. Thread the membrane cap onto the sensor. It is normal for a small amount of electrolyte to overflow.

Installing and Uninstalling Sensors

GENERAL PRECAUTIONS

It is important that the entire sensor connector and cable connector be dry when installing, removing or replacing sensors. This will prevent water from entering the port. Once a sensor is removed, examine the connector inside the port. If any moisture is present, use compressed air to completely dry the connector or place directly in front of a steady flow of fresh air. If you suspect port contamination, follow the port cleaning procedures listed under Cleaning a Sensor Port.

Remove sensors upside down (facing the ground) to help prevent water from entering the port upon removal.

The instrument utilizes o-rings as seals to prevent water from entering the sensor ports. When the sensors are removed, the o-rings that provide the seal should be carefully inspected for contamination (e.g. debris, grit, etc.) and cleaned if necessary.

If no dirt or damage to the o-rings is evident, wipe the o-rings with a lint free cloth or lens cloth to remove the old o-ring grease. Then, lightly apply new o-ring grease (provided in the maintenance kit) to the o-rings without removing them from their groove. If there is any indication of damage, the o-ring should be replaced with an identical o-ring. At the time of o-ring replacement, the entire o-ring assembly should be cleaned.

Do not over-grease the o-rings. The purpose of the o-ring grease it to keep the o-ring in good condition. Excess grease may collect grit particles that can compromise the seal. Excess grease can also cause the waterproofing capabilities of the o-ring to diminish, potentially causing leaks. If excess grease is present, remove it using a lens cloth or lint-free cloth.

To remove the o-rings:
Use a small, flat-bladed screwdriver or similar blunt-tipped tool to remove the o-ring from its groove. Do not use a sharp object to remove the o-rings. Using a sharp object could damage the o-ring groove which would allow water to enter the port resulting in permanent damage to the port and sensor. Check the o-ring and the groove for any excess grease or contamination. If contamination is evident, clean the o-ring and nearby plastic parts with lens cleaning tissue or equivalent lint-free cloth. Alcohol can be used to clean the plastic parts, but use only water and mild detergent on the o-ring itself. Using alcohol on o-rings may cause a loss of elasticity and may promote cracking. Also, inspect the o-rings for nicks and imperfections.

Before re-installing the o-rings, make sure to use a clean workspace, clean hands, and avoid contact with anything that may leave fibers on the o-ring or grooves. Even a very small amount of contamination (hair, grit, etc.) may cause a leak.

To re-install the o-rings:
Place a small amount of o-ring grease between your thumb and index finger. Draw the o-ring through the grease while pressing the fingers together to place a very light covering of grease to the o-ring. Place the o-ring into its groove making sure that it does not twist or roll. Do no excessively stretch the o-ring during installation.

Use your grease-coated finger to once again lightly go over the mating surface of the o-ring.

Do not over-grease the o-rings. The excess grease may collect grit particles that can compromise the seal. Excess grease can also cause the waterproofing capabilities of the o-ring to diminish, potentially causing leaks. If excess grease is present, remove it using a lens cloth or lint-free cloth.

UNINSTALLING DO, PH, ORP, PH/ORP AND ISE SENSORS

First, ensure that the entire sensor and cable bulkhead are clean and dry. Remove sensors upside down (facing the ground) to help prevent water from entering the port upon removal.

Simply unscrew the sensor from the cable by holding the sensor port end of the cable (bulkhead) in one hand and the sensor in the other hand. Twist the sensor counter-clockwise to unscrew the sensor from the port.

INSTALLING DO, PH, ORP, PH/ORP AND ISE SENSORS

First, ensure both the sensor connector and sensor port on the cable are clean and dry. If any moisture is present, use compressed air to completely dry the connector or place directly in front of a steady flow of fresh air. If you suspect port contamination, follow the port cleaning procedures listed under Cleaning a Sensor Port.

To connect the sensor, grasp the sensor with one hand and the sensor port end of the cable (bulkhead) in the other. Push the sensor into the connector on the cable until it is properly seated and only one o-ring is visible. Failure to properly seat the sensor may result in damage. Twist the sensor clockwise to engage threads and finger tighten. Do not use a tool. This connection is waterproof. Please refer to the sensor installation sheet that is included with each sensor for detailed instructions.

UNINSTALLING A CONDUCTIVITY/TEMPERATURE SENSOR IN A QUATRO CABLE

First, ensure that the entire sensor and cable bulkhead are clean and dry. Remove sensors upside down (facing the ground) to help prevent water from entering the port upon removal.

Remove the conductivity/temperature sensor using the installation tool to loosen the stainless steel retaining nut. Insert the tool into one of the holes in the stainless steel retaining nut. Next, use the installation tool to turn the stainless steel retaining nut counter-clockwise to loosen. Do not allow the sensor to be turned with the tool. Turning the sensor with the tool will likely damage the sensor connector. Once the stainless steel retaining nut has been completely loosened from the bulkhead, remove the sensor from the bulkhead by pulling the sensor straight out of the port.

INSTALLING A CONDUCTIVITY/TEMPERATURE SENSOR IN A QUATRO CABLE

First, ensure both the sensor connector and sensor port on the cable are clean and dry. If any moisture is present, use compressed air to completely dry the connector or place directly in front of a steady flow of fresh air. If you suspect port contamination, follow the port cleaning procedures listed under Cleaning a Sensor Port.

1. Align the connectors of the sensor and the port. With connectors aligned, push the sensor in towards the bulkhead until you feel the sensor seat in its port. You will experience some resistance as you push the sensor inward, this is normal
2. Once you feel the sensor seat into the port, gently rotate the stainless steel sensor nut clockwise with your fingers, do not use the tool.
3. The nut must be screwed in by hand. If the nut is difficult to turn, STOP, as this may indicate cross threading. If you feel resistance or cross threading at any point, unscrew the nut and try again until you are able to screw the nut down completely without feeling any resistance. Damage to your cable/sensor may occur if you force the parts together.
4. Once completely installed, the nut will seat flat against the bulkhead. At this point, use the installation tool that was included with the sensor to turn the nut an additional ¼ to ½ turn. Do not over tighten.
5. Please refer to the sensor installation sheet that is included with the conductivity/temperature sensor for detailed instructions.

Cleaning a Sensor Port

If you suspect port contamination, you can clean the port on the cable by filling the port with Isopropyl Alcohol for 30 seconds and then dumping it out. Next, allow the port to air dry completely or blow it out with compressed air. Installing a sensor into a port that is not completely dry is likely to cause erratic and erroneous readings.

If the connector is corroded, contact your local YSI Representative or a YSI Authorized Service Center.

Verifying Sensor Accuracy and Calibration

Sensor accuracy and calibration can be verified by immersing a sensor into calibration solution or YSI Confidence Solution®. Compare the readings on the Pro Plus display to the value of the solution. If the readings have drifted more than the accuracy specification of the sensor, perform a calibration before taking field measurements.

YSI Confidence Solution can be used to check the accuracy and calibration of the conductivity, pH and ORP sensors. However, to maintain the highest accuracy of the instrument, it should not be used to perform a calibration.

Resetting a Sensor to Factory Default

Occasionally, it may be necessary to reset the instrument to its factory calibration default values. To reset the calibration values, press the Cal key (Cal), highlight **Restore Default Cal** and press enter. Highlight the parameter you wish to reset to default and press enter. Next, you will be asked to confirm the operation. Highlight **Yes** and press enter to confirm.

Use the ▲ or ▼ keys to set user number from 0-99. Use the **READ** or **SAVE** button to set the user number and exit to the ID menu.

3.2.2 Calibrate

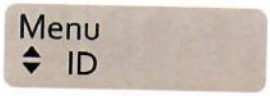
From the main menu, use the ▲ or ▼ keys select the Calibrate function, then press **READ** to enter that submenu.

The Standard vials must be thoroughly cleaned before each measurement, using a lint-free cloth.

Guided Cal.

The complete calibration procedure, as outlined below, should be performed by the user according to required quality and maintenance programs.

1. Gather the four (4) calibration sample vials with formula standards of <0.10 (i.e. 0.02), 20.0, 100, 800 NTU (or stabilized primary standards in the same concentrations).
   - Ensure each vial is cleaned with a soft cloth.
2. Hold **MENU** button for 3 seconds until the main menu is displayed.



3. Scroll through the menu using the ▲ or ▼ keys until "Calibrate" is displayed.
4. Press the **READ** button to enter into the calibration menu.
5. Select "Guided Cal" and follow the scrolling prompts on the screen.
   - Before placing each vial into the sample chamber, gently invert the vial to ensure a homogeneous mix.
6. Once done calibrating to the four standards, the instrument will return to the calibration menu.
7. Press the **ESC** key twice to navigate to the ready-to-sample screen.

Free Cal.

Free Calibration allows for a single calibration point. For many users, this single point calibration will be sufficient for routine work.

1. Follow steps 1-3 from "Guided Cal" above.
2. Select "Free Cal"
3. On the "Cal. Auto" screen, there will be a value displayed from the previous calibration. Place one of the calibration standards into the sample chamber.

4. Press READ button and wait for result.

5. If necessary use ▲ or ▼ keys to change the displayed value for this standard to match its label, press and hold **SAVE** for 3 seconds.
   - "Saving" will be displayed.

6. After the value is saved, the display returns to the "Calibrate" menu.

7. Recalibrate against the same standard for better accuracy, or perform the "Guided Cal" routine.

NOTE 1: If an error message displays, check the standards and repeat the previous steps.

NOTE 2: After the calibration, perform standard readings for verification, and if needed repeat the calibration procedure.

Section 3: System Operation

Turn the ET WLM on with the ON/SENSITIVITY switch. If the buzzer makes a loud signal and a red light is visible, the battery is adequate for normal operation.

Lower the probe down the well to the water surface. The light and buzzer will activate. At this point, adjust the probe dial by rotating it counter-clockwise until the light and buzzer turn off.

With the probe still in contact with the water, adjust the probe sensitivity dial clockwise until the light and buzzer barely activate. In this setting, the probe will detect the water level and avoid false triggering.

Water level measurements can now be taken from the top of the casing or any reference point.

The ET WLM should be stored with the ON/SENSITIVITY switch in the OFF position. To turn the unit off, rotate the switch fully counter-clockwise until the switch clicks. If the ET WLM is not used and is stored for longer than three (3) months, remove the battery to prevent battery leakage, which can cause internal damage.

To avoid damage to the tape and strain relief, do not over tighten the reel with the probe in storage position.

This unit is not rated for use with hydrocarbons or flammable liquids. If measuring depth to fluid of wells containing hydrocarbons, use Geotech's line of interface probe products.

Operation of Optional Draw Down Control

1. Lower the probe to desired depth of maximum allowable draw down with the unit in standard ET WLM mode (switch at "Right") – see Figure 1-3.

2. Move the mode switch to the "Left ", for Draw Down mode.

3. Connect the ET WLM to a controller; such as the Geotech GeoControl Pro or Geo Controller, which is equipped with a Draw Down feature, as shown in Figure 1-3.

4. Operate your controller in accordance with the controller's operation manual. The ET WLM will stop the controller when the water level dips below it. It will allow the controller to re-start when the water level rises and makes contact with the probe

Attachment 4

PFAS Compound List

USEPA PFAS Method 537 Modified List - RACER Pontiac North Campus

1. 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)
2. 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3ONS)
3. 1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)
4. 1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)
5. 1H,1H,2H,2H-perfluorohexane sulfonic acid (4:2 FTS)
6. Hexafluoropropylene oxide dimer acid (GenX)
7. 4,8-dioxa-3H-perfluorononanoic acid (ADONA)
8. N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA)
9. N-methylperfluoro-1-octanesulfonamidoacetic acid (MeFOSAA)
10. Perfluoro-1-butanesulfonic acid (PFBS)
11. Perfluoro-1-decanesulfonic acid (PFDS)
12. Perfluoro-1-heptanesulfonic acid (PFHpS)
13. Perfluoro-1-nonanesulfonic acid (PFNS)
14. Perfluoro-1-octanesulfonamide (PFOSA)
15. Perfluoro-1-pentanesulfonic acid (PFPeS)
16. Perfluorohexanesulfonic acid (PFHxS)
17. Perfluoro-n-butanoic acid (PFBA)
18. Perfluoro-n-decanoic acid (PFDA)
19. Perfluoro-n-dodecanoic acid (PFDoA)
20. Perfluoro-n-heptanoic acid (PFHpA)
21. Perfluoro-n-hexanoic acid (PFHxA)
22. Perfluoro-n-nonanoic acid (PFNA)
23. Perfluoro-n-octanoic acid (PFOA)
24. Perfluoro-n-pentanoic acid (PFPeA)
25. Perfluoro-n-tetradecanoic acid (PFTeDA)
26. Perfluoro-n-tridecanoic acid (PFTrDA)
27. Perfluoro-n-undecanoic acid (PFUdA)
28. Perfluorooctanesulfonic acid (PFOS)

Attachment 5

Laboratory Standard Operating Procedure for Modified USEPA Method 537M

1.0 Scope And Application

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) with Isotope Dilution Quantification in aqueous and solid matrices.

The requirements outlined in this SOP conform to those presented in Table B-15 of the Department of Defense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories. Table B-15 requirements are included in Appendix H for reference. Additional appendices are included for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in Appendix A.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 Summary of Method

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

2.1 **PFAS Isotope Dilution method (aqueous; ID-AQ)** - A 250-mL water sample is fortified with surrogates (SUR; also referred to as extracted internal standards [EIS] or isotope dilution standards [IDS]) and passed through a stacked Polymeric Weak Anion Exchange (WAX)/Graphitized Carbon (GCB) SPE/filtration cartridge (Phenomenex Strata-PFAS (WAX/GCB), or equivalent) to extract the method analytes and SUR. The compounds are eluted from the SPE cartridge with 4-mL of methanol and 4-mL of ammonia-methanol (0.6%), with a separate final cartridge rinse of 2-mL of clean MeOH. With the final cartridge rinse, the extract volume is approximately 10 mL. Sample extracts are concentrated in a heated water bath under nitrogen to final volume of either 5mL or 2mL, depending on project objectives. A 10 µL aliquot of the concentrated extract is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the 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 isotope dilution technique.

2.2 **PFAS Isotope Dilution method (solid; ID-Solid)** - Approximately 1g of solid sample is spiked with SUR/EIS/IDS and mixed with 4mL of methanol and 4mL of ammonia-methanol (0.6%). The spiked sample with extraction solvent is then shaken on an orbital shaker, followed by sonication and centrifugation. The extract is filtered by SPE (Strata-GCB or equivalent), with a tube rinse of 2-mL of clean MeOH. The extract volume following the filtration step is approximately 10 mL. Sample extracts are concentrated in a heated water bath under nitrogen to final volume of either 5mL or 2mL, depending on project objectives. A 10 µL aliquot of the concentrated extract is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the 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 isotope dilution technique. See Appendix B for specific procedures for preparing and analyzing solid samples by ID-Solid.

2.3 **PFAS Isotope Dilution method (Aqueous Serial Dilution; ID-SD)** - Samples of known high PFAS concentrations, such as AFFF pure product formulations, can be prepared by serial dilution instead of SPE, with documented project approval. The sample serial dilutions will be prepared in 96% MeOH: 4% water. SUR will be spiked into the diluted sample (not the original sample collected) in the preparation vial. Any target analytes found to be ND in any samples shall be spiked at the LOQ level (post-spike) in those samples at the dilution reported and analyzed again. Recovery for the post-spiked analytes must fall within 70-130% of the expected value; if these criteria are not met, the post-spike analysis will be repeated at successively higher dilutions until recovery is acceptable. The spiking concentration will be used to calculate the project specific LOQ for each analyte. 10-µL of the prepared dilution aliquot is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the 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 isotope dilution technique. See Appendix E for specific procedures for preparing and analyzing serial dilution samples by ID-SD.

3.0 Interferences

3.1 Non-volumetric glassware can be solvent rinsed or heated in a muffle furnace at 400°C for 2-hours. Volumetric glassware should be solvent rinsed and can be heated in an oven at a temperature below 120°C. Store clean glassware inverted or capped. Do not cover with aluminum foil since PFAS may potentially be transferred from the aluminum foil to the glassware.

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

3.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample containers and caps, and other sample processing equipment that lead to discrete artifacts and/or elevated baselines in the chromatograms. Method analytes may 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. Supplies and equipment are demonstrated to be free from interference (no analyte detected > ½ LOQ) by evaluation of routine method blanks (MB). Subtracting blank values from sample results is not permitted.

3.3 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.

3.4 SPE cartridges/tubes 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 sorbent lots of SPE devices should be tested to ensure that contamination does not prevent analyte identification and quantitation.

4.0 Definitions

Refer to the Laboratory Quality Manual [QAMP ME0012K] for a glossary of common lab terms and definitions.

4.1 **Collisionally Activated Dissociation (CAD)** – The process of converting the precursor ion's translational energy into internal energy by collisions with neutral gas molecules to bring about dissociation into product ions.

4.2 **Surrogate/Extracted Internal Standard/Isotope Dilution Standard (SUR/EIS/IDS)** – A pure chemical which chemically resembles method analytes and is extremely unlikely to be found in any sample. This chemical is added to a sample aliquot (field and QC) in known amount(s) before the extraction and analysis processes. The purpose of the SUR is to monitor method performance from extraction to final chromatographic measurement. For the ID methods, the SUR is used as an isotope dilution standard for measuring the relative response and quantification of other method analytes.

4.3 **Field Duplicates (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.

4.4 **Precursor Ion** – The precursor ion is typically the deprotonated molecule ([M-H]-) of the method analyte. In MS/MS, the precursor ion is the mass selected and fragmented by collisionally activated dissociation to produce distinctive product ions of smaller m/z.

4.5 **Product Ion** – A product ion is one of the fragment ions produced in MS/MS by collisionally activated dissociation of the precursor ion.

4.6 **Non-conformance Memo (NCM)** - A form used to document a non-conforming event. An analyst must document a non-conformance memo when a non-conforming event occurs. A non-conforming event may include the reporting of analytical data outside of method or SOP criteria, or when there is a deviation from a written policy or procedure. Information in an NCM may be used by project managers to flag data in the report narrative, or by the quality department to track trends and initiate corrective actions, where applicable. Additional information on the NCM policy and procedure is located in the Nonconformance and Corrective Action SOP [QA SOP ME0012BO].

4.7 **Minimum Reporting Level (MRL) [WI DNR Compliance]** - The minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. This 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. Synonymous with Limit of Quantitation (LOQ).

5.0 Health And Safety

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 Sample Collection, Preservation, Holding Time, And Storage

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with the *Field Services* SOP [FS SOP ME001BS]. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with the *Sample Container Shipping* SOP [AD SOP ME001DS].

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are listed in the *Pace-WCOL Analytical Methods List* [ME002BS].

General Requirements

Matrix	Routine Container	Min. Sample Amount[1]	Preservation	Holding Time
Aqueous	250 mL HDPE bottle fitted with polyethylene screw-cap lid	250 mL	**Thermal:** ≤ 10°C[2] **Chemical:** None	**Collection to Prep:** 28 days **Prep to Analysis:** 28 days
Solid	4 oz. HDPE bottle fitted with polyethylene screw-cap lid	10 g	**Thermal:** ≤ 10°C **Chemical:** None	**Collection to Prep:** 28 days **Prep to Analysis:** 28 days

[1]*Minimum amount needed for each discrete analysis.*
[2]*For Wisconsin compliance, samples must be received at above their freezing point to 6°C*

Field / Matrix QC

Trip Blank	MS/MSD	Field Duplicate

Analysis of TB required only if sample contains analyte concentrations at or above the LoQ.[1]	Analysis of an MS is required in each extraction batch. Assessment of method precision can be accomplished by analysis of a FD; however, infrequent occurrence of method analytes might hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, an MSD must be analyzed. Extraction batches that contain MSD will not require the extraction of an FD.	Within each extraction batch a minimum of one FD or MSD must be analyzed. If method analytes are not routinely observed in field samples, an MSD should be analyzed rather than an FD.

[1] Lab analyzes all TB, regardless of sample concentration.

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with the *Sample Receiving* SOP [AD SOP ME0013H]. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at 4±2°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at room temperature until sample analysis.

NOTE: Wisconsin compliance sample extracts will be stored at 0-6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 Equipment And Supplies

7.1 Equipment

NOTE: Refer to the Major Operational Equipment List [QA Control Log ME001PM] for specific details regarding the equipment and data processing software utilized during this procedure.

NOTE: Due to the possibility of adsorption of analytes onto glass, HDPE containers are used for all standard, sample and extraction preparations. Any time a new lot of SPE cartridges/tubes, solvents, cryovials, or autosampler vials are used, it must be demonstrated that a MB is reasonably free of contamination and that the criteria in Section 11.4.1 are met.

7.1.1 **Analytical Balance** – Capable of weighing to the nearest 0.0001 g

7.1.2 **Point of Use water preparation system –** Millipore Direct-Q 8 UV

7.1.3 **Solid Phase Extraction (SPE) Apparatus**

7.1.3.1 Stacked SPE/filtration cartridges: Strata PFAS(WAX/GCB), 500mg/50mg/6mL, Phenomenex part# CS0-9208, or equivalent

7.1.3.2 25mg GCB pass-through filtration cartridges (for solid extract clean-up): Strata GCB 25mg/1mL Cartridge, Phenomenex part# 8B-S528-CAJ

7.1.3.3 Vacuum Extraction Manifold – VisiPrep 24-port SPE manifold, Millipore-Sigma part# 57265, or equivalent. Care must be taken with automated SPE systems to ensure the PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the MB.

7.1.3.4 Disposable liners for Visiprep Manifold – Millipor-Sigma part# 57059 / Restek part# 28310-VM, or equivalent.

7.1.3.5 SPE reservoirs – 60 mL and 12 mL polypropylene, Phenomenex part# AH0-7189 and AH0-7003, or equivalent.

7.1.3.6 SPE adapter caps – Phenomenex Part# AH0-7191 (Adapter cap for 1, 3, 6mL SPE tubes)

7.1.3.7 Vacuum tubing – 1/4" ID, 5/8" OD, 3/16" wall; Fisher Scientific part# 14-176-6B or equivalent

7.1.4 **Vacuum Pump** – Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury for extraction cartridges. Millipore model# WP6111560, 115V, 60Hz, 3.5A.

7.1.5 **Liquid Chromatography (LC)/Tandem Mass Spectrometer (MS/MS) with Data System**

7.1.5.1 LC System – Agilent Model 1260, with Degasser (G4225A), Binary Pump (G1312B), Autosampler (G1329B), Thermostat (G1330B), Column Compartment (G1316A).
Shimadzu Model LC-30AD, with Communication Bus Module (CBM-20A), Column Oven (CTO-30A), Degassing Unit (DGU-20A5R), Autosampler (SIL-20AC XR).

NOTE: PFAS can build up in the PTFE solvent transfer lines and PTFE solvent frits. To prevent long delays in purging high levels of PFAS from the LC solvent lines, PEEK tubing and stainless-steel frits are used.

7.1.5.2 Tandem Mass Spectrometer (MS/MS) – Sciex 4500 or 5500 MS/MS, in negative ion electrospray ionization (ESI) mode. A minimum of 10 scans across the chromatographic peak is required to ensure adequate precision.

7.1.5.3 Analytical Column – Phenomenex Gemini® 3µm C18 110Å LC column 50 x3mm, (part# 00B-4439-Y0). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision may be used.

7.1.5.4 Mixing/Delay Column – Phenomenex Luna 5µm C18 100Å LC column 30 x 3mm (part# 00A-4252-Y0) or equivalent.

7.1.5.5 Guard cartridge – SecurityGuard Cartridges: Gemini C18, 2-3mm ID, 10/pk; Part# AJ0-7596/AJ0-7597; Phenomenex Part# KJ0-4282 (SecurityGuard Guard Cartridge Kit)

7.1.6 **Extract Concentration System** – Extracts are concentrated by evaporation with nitrogen using a water bath set to 55-60 °C (TurboVap LV, Biotage Inc, or equivalent).

7.1.7 **Vortex Mixer** - Bibby Scientific/Stuart Vortex Mixer, Model SA8, or equivalent.

7.1.8 **Orbital shaker table** - VWR Model 3500 Standard Shaker, 120V, or equivalent

7.1.9 **Centrifuge** - VWR Clinical 200, Hettich Rotanta 460, or equivalent

7.1.10 **Sonicator** - VWR Model 97043-976, or equivalent

7.1.11 **Kimwipes –** Fisher Scientific part # 06-666A, or equivalent

7.2 Supplies

7.2.1 **Extract/Standard storage containers** – 15-mL, 8-mL, or 4-mL narrow-mouth HDPE container - Thermo Scientific item# 2002-9050, 2002-9025, 2002-9125; 2.0-mL screw-top polypropylene

cryogenic vials – Grainger item# 6EMV1;1.5-mL snap-cap polypropylene microcentrifuge tubes - Fisher item# 05-408-129; or equivalent.

7.2.2 **Centrifuge Tubes** – 15-mL conical polypropylene tubes with or without (MoldPro) polypropylene screw caps for preparing and storing extract solutions and for collection of eluents (VWR catalogue# 10026-076 or equivalent; MoldPro, Inc. item# MP-100, 17x100mm sample tubes or equivalent - alternate extract collection tubes). 500-mL conical polypropylene bottles with polypropylene screw caps for centrifuging aqueous samples containing high solids content (Fisher catalogue# 07-200-621 or equivalent).

7.2.3 **Autosampler Vials** – Polypropylene vials (Agilent part# 5188-2788) with polypropylene caps (Agilent part# 5182-0542), or equivalent.

NOTE: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa. However, polypropylene caps do not reseal, so evaporation occurs after injection. Thus, multiple injections from the same vial are not advisable.

7.2.4 **Micropipettes** – Range of volumes (see section 8 for volumes needed)

7.2.5 **Plastic Pipettes** – Polypropylene or polyethylene disposable pipettes, Fisher Cat# 13-711-7M or equivalent.

7.2.6 **Ottawa Sand** - for solid QC preparation (VWR catalog #: EM-SX0075-3 or equivalent)

8.0 Reagents And Standards

NOTE: Reagent grade or better chemicals should be used. Unless otherwise indicated, it is intended that ACS reagents be used, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the analysis.

8.1 Reagents

8.1.1 **Reagent Water** – Optima LC/MS water, Fisher part# W6-4 or equivalent.

8.1.1.1 The reagent water should not contain any measurable quantities of any method analytes or interfering compounds greater than 1/2 the LOQ for each analyte of interest.

8.1.2 **Methanol (MeOH, CH3OH, CAS#: 67-56-1)** – HPLC grade, demonstrated to be free of analytes and interferences (Fisher part# A452-4 or equivalent).

8.1.3 **Ammonium Acetate (NH4C2H3O2, CAS#: 631-61-8)** – LC/MS grade (Fisher part# A114-50 or equivalent).

8.1.4 **20 mM Ammonium Acetate** – To prepare 1 L, add 1.54 g ammonium acetate to 1L of reagent water (0.77g into 0.5L reagent water). This solution is prone to volatility losses and should be replaced at least every 96 hours.

8.1.5 **Ammonium Hydroxide (NH4OH, CAS#: 1336-21-6)** – ACS Plus grade (Fisher part# A669C-212 or equivalent)

8.1.6 **Ammonia-Methanol (Amm-MeOH, 0.6%)** – In a 1000 mL graduated cylinder, add 20 mL NH4OH (Ammonium Hydroxide) and fill to volume with methanol (980 mL reagent MeOH). Invert to mix.

8.1.7 **Ammonium Acetate/Acetic Acid buffer (25mM, pH 4)** – In a 2000 mL volumetric flask, add 2.32 mL acetic acid and 0.80 g ammonium acetate then fill to volume with reagent water (1997.68 mL reagent water). Invert to mix.

8.1.8 **Nitrogen** – Nitrogen aids in aerosol generation of the ESI liquid spray and is used as collision gas in some MS/MS instruments. The nitrogen used should meet or exceed instrument manufacturer's specifications.

8.2 Standards

NOTE: When a compound purity is assayed to be 96% or greater (standards purchased from Wellington are >98%), the weight can be used without correction to calculate the concentration of the stock standard. PFAS analyte, IS, and SUR 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. Solution concentrations listed in this section were used to develop this method and are included as an example. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples.

NOTE: The final compositions for all standards in section 8.2 contain 96:4% (v/v) methanol/water. The solutions are stored at 2-6°C in HDPE containers, except for the solutions in 8.2.8, 8.2.11, and 8.2.16.2, which are routinely stored at room temperature.

8.2.1 **Surrogate (SUR) Stock Standard Solutions –** The SUR standard stocks are obtained from Wellington Labs (catalog #s: M2PFHxDA, M2-4:2FTS, M2-6:2FTS, M2-8:2FTS, M8FOSA-I, d-N-EtFOSA-M, d-N-MeFOSA-M, d5-N-EtFOSAA-M, d3-N-MeFOSAA-M and MPFAC-C-ES). SUR stock standard solutions are stable for at least 12 months when stored at 2-6°C.

8.2.2 **SUR 50X Mix** - Dilute the stock standards with methanol/water in accordance with the table below:

SUR 50X Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] hexane sulfonate (13C2-4:2FTS)	50	1000	10	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] octane sulfonate (13C2-6:2FTS)	50	1000	10	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] decane sulfonate (13C2-8:2FTS)	50	1000	10	5.0
Perfluoro-1-[$^{13}C_8$] octanesulfonamide (13C8-PFOSA)	50	200	10	1.0

N-ethyl-d5-perfluoro-1-octanesulfonamide (d5-EtFOSA)	50	200	10	1.0
N-methyl-d3-perfluoro-1-octanesulfonamide (d3-MeFOSA)	50	200	10	1.0
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-EtFOSAA)	50	1000	10	5.0
N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-MeFOSAA)	50	1000	10	5.0
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-$^{13}C_3$-propanoic acid (13C3-GenX)	50	1000	10	5.0
2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)	50	200	10	1.0
2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)	50	200	10	1.0
Perfluoro-n-[1,2-$^{13}C_2$] hexadecanoic acid (13C2-PFHxDA)	50	200	10	1.0

8.2.3 **100 ppb SUR Mix** - Combine the SUR 50X mix and Wellington Labs standard part# MPFAC-C-ES and dilute with methanol/water in accordance with the table below:

100 ppb SUR Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
SUR 50X Mix	1	2200	22	0.10
MPFAC-C-ES Stock	2	1100	22	0.10

NOTE: The complete list of compounds included in the ID (Aqueous and Solid) 100 ppb SUR Mix is found under Table 5.

8.2.4 **Analyte Primary Dilution Standards (PDS)** – Analyte standards are purchased from Wellington Labs as ampoulized solutions. The PDS standards are stable for at least 12 months when stored at 2-6°C.

8.2.4.1 PFHxS, PFOS and other sulfonic acids are not available as the acid form, but rather as their corresponding salts, such as Na+ and K+. These salts are acceptable for use as stock standards as long as the weight is corrected for the salt content according to the equation below.

$$Mass_{acid} = Measured\ Mass_{salt} \times \frac{MW_{acid}}{MW_{salt}}$$

Where:
MW_{acid} = the molecular weight of PFAA
MW_{salt} = the molecular weight of purchased salt

8.2.5 **10X Stock Analyte PDS** – Contains all target analytes at 0.2 ug/mL, except GenX which is present at 0.4 ug/mL (GenX is present in PFAC-30PAR; additional spike of individual stock standard is added to give double concentration). Prepare as outlined below:

8.2.5.1 2 mL of the primary lot of PFAC-30PAR standard mix, 40 uL of MeFOSA, EtFOSA, 10:2 FTS, MeFOSE, EtFOSE, GenX, PFDOS, PFHxDA, and PFODA primary standards, are diluted to 10 mL with methanol and reagent water, for a final composition of 96%MeOH.

8.2.6 **100X Analyte PDS** - Contains all target analytes at 20 ng/mL, except GenX which is present at 40 ng/mL. Prepare as outlined below:

8.2.6.1 1 mL of Stock (10X) Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

8.2.7 **1000X Analyte PDS** - Contains all target analytes at 2.0 ng/mL, except GenX which is present at at 4.0 ng/mL. Prepare as outlined below:

8.2.7.1 1 mL of 100X Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

8.2.8 **Initial Calibration Standards (ICAL)** – According to the table below, prepare calibration standards at the following nominal concentrations in pg/mL (ng/L): 50, 100, 200, 500, 1000, 2000, 5000, 10000, 15000 and 20000, except for GenX which will be at double these concentrations. The ICAL standards are stable for at least three months when stored at room temperature, or 12 months when stored at 2-6°C. See Table 5 for a list of analytes and exact concentrations.

ICAL Preparation (Aqueous)							
ICAL Level	**PFAS Conc. (pg/mL)**	**SUR Conc. (pg/mL)**	**PFAS PDS 10X (mL)**	**PFAS PDS 100X (mL)**	**PFAS PDS 1000X (mL)**	**100 ppb SUR (mL)**	**Final Volume (mL)**
1	50	2000	-	-	0.125	0.1	5
2	100	2000	-	-	0.250	0.1	5
3	200	2000	-	-	0.500	0.1	5
4	500	2000	-	0.125	-	0.1	5
5	1000	2000	-	0.250	-	0.1	5
6	2000	2000	-	0.500	-	0.1	5
7	5000	2000	0.125	-	-	0.1	5
8	10000	2000	0.25	-	-	0.1	5
9	15000	2000	0.375	-	-	0.1	5
10	20000	2000	0.50	-	-	0.1	5

NOTE: ICAL preparation procedures are subject to change without notice

8.2.9 **10X ICV PDS mix** – Second source standard containing required target analytes at 0.2 ug/mL or 200ppb, except those compounds not contained in the PFAC-24PAR stock mix, which are present at a nominal concentration of 1.0 ug/mL or 1000ppb. Prepare as outlined below:

8.2.9.1 Dilute PFAC-24PAR standard mix (secondary source/preparation) and 40uL each of GenX, ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUDS secondary standards are diluted to 2mL with methanol and water, for a final solvent composition of 96:4% MeOH:water. The PFAC-24PAR standard includes all analytes listed in Table 5 except the following: GenX, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUDS, 10:2FTS, MeFOSA, EtFOSA, MeFOSE, EtFOSE, PFDOS, PFHxDA, and PFODA.

8.2.10 **100X ICV Mix** - Second source standard containing required target analytes at 0.02 ug/mL or 20ppb. Prepare as outlined below:

8.2.10.1 Dilute 0.5 mL of the 10X ICV PDS mix to 5mL using 96:4% MeOH:water.

8.2.11 **ICV Sample Solution (500ppt)** – Prepare according to the table below. Note: secondary standards for the following compounds are not included in the ICV sample: 10:2 FTS, MeFOSA, EtFOSA, MeFOSE, EtFOSE, PFDOS, PFHxDA, PFODA

ICV Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (pg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (pg/mL)**
PFAS ICV 100X Mix	20000	25	1.0	500
Full List SUR mix, 100ppb	100000	20	1.0	2000

8.2.12 **Isomer check** – For target compounds which have multiple chromatographic peaks due to branched and linear isomers, but for which quantitative standards are not available, a qualitative check is analyzed with each calibration event to demonstrate the peak shape and retention time of the branched isomers. See sections 10.5, 10.6 for integration information.

8.2.12.1 **Isomer Check 50X Mix** – 20 µL each of TPFOA, br-MeFOSAA, and br-EtFOSAA standards (Wellington Laboratories item #s T-PFOA, br-MeFOSAA, and br-EtFOSAA) are diluted to 1 mL with 900 µL of MeOH and 40 µL of reagent water. Final solvent composition is 96:4% MeOH:water. This solution is used to create the actual isomer check standard to be analyzed with each ICAL. Note: branched/linear isomer mixes of MeFOSAA and EtFOSAA are now present in the analyte PDS solutions, so these compounds will be calibrated with branched and linear isomers summed, but will also continue to be present in the Isomer Check mix.

8.2.12.2 **Isomer Check Standard** - 10 µL of the Isomer Check 50X Mix plus 20 µL of the 100 ppb SUR are diluted to 1 mL with 96% MeOH. The concentrations of the isomer components should be approximately 10000 ppt. This sample will be analyzed with each calibration event to demonstrate peak shape and retention time of the additional branched isomers of the included compounds.

8.2.12.3 As more qualitative standards containing mixes of branched and linear isomers become commercially available, the lab will add those newly available compounds/standards to the isomer check mix and analyze them in the manner described in Sec. 8.2.12.

8.3 Instrument Blank (IBLK) – The instrument blank is prepared by spiking 942 µL of MeOH and 38 µL of Water with 20 µL of SUR 100ppb; cap and vortex to mix, then aliquot into auto-sampler vial.

8.4 Method Blank (MB) – For 5mL FV extracts, spike 250 mL reagent water with 100 µL of the 100ppb SUR Mix. Mix well, extract as normal alongside client samples. For 2mL FV extracts, spike 250 mL reagent water with 40 µL of the 100ppb SUR Mix. Mix well, extract as normal alongside client samples.

9.0 Procedure

9.1. Equipment Preparation

9.1.1 Support Equipment

9.1.1.1 Refrigerator units are maintained and verified as required by the Quality Assurance Management Plan [QAMP ME0012K].

9.1.1.2 The balance is verified at the beginning of each analytical day using a certified weight set. Refer to the Equipment and Instrumentation SOP [QA SOP ME002JT] for balance verification procedures and acceptance criteria.

9.1.1.3 Bottletop dispensers, pipettes, and thermometers are maintained and verified as required by the Equipment and Instrumentation SOP [QA SOP ME002JT].

9.1.2 Instrument

9.1.2.1 Example Chromatographic Conditions

Step	Total Time (min)	Flow Rate (uL/min)	A: 20mM Ammonium Acetate (%)	B: Methanol (%)
0	0.00	1200	95.0	5.0
1	0.10	1200	45.0	55.0
2	4.50	1200	1.0	99.0
3	6.00	1200	1.0	99.0
4	6.10	1200	95.0	5.0
5	8.10	1200	95.0	5.0

9.1.2.2 Example Mass Spectrometric Conditions

Parameter	Setting or Value
Syringe Size	100 µL
Injection Volume	10 µL
Draw Speed	50.0 µL/min
Eject Speed	50.0 µL/min
Needle Level	3.0 mm
Column Oven Temperature	40°C
MRM Scan Window	60 sec
Curtain Gas (CUR)	30.0
Collision Gas (CAD)	9
Ion Spray Voltage (IS)	-4500.0 V
Temperature (TEM)	450.0°C
Ion Source Gas 1 (GS1)	40.0

Ion Source Gas 2 (GS2)	60.0

9.2. Initial Calibration

9.2.1 Mass Calibration – calibrate the mass scale of the MS with the calibration compounds and procedures prescribed by the manufacturer. Mass calibration/mass tune will be performed any time major maintenance is performed on the MS, or following any catastrophic instrument failure (power loss, etc.)

9.2.2 Mass Calibration verification – a mass calibration verification will be analyzed following mass calibration/mass tune, prior to initial calibration (ICAL). A prepared standard containing PFAS targets will be injected using the normal LC parameters for analysis but set up to perform a product ion (MS2) scan for the quantitation product ions of PFOA (m/z 369) and PFOS (m/z 80). If these target product ions are detected at the expected RT, the mass calibration has been verified.

9.2.3 Prepare a set of at least five ICAL standards (six ICAL standards for quadratic regressions) as described in Section 8. The lowest concentration ICAL standard must be at or below the LOQ, which may depend on system sensitivity. It is recommended that at least four of the ICAL standards are at a concentration greater than or equal to the LOQ.

9.2.4 The LC/MS/MS system is calibrated using the IS technique. A calibration curve for each of the analytes is generated by average response factor (AVG RF) or linear regression. Linear regression curves may be concentration weighted, if necessary. Linear or quadratic calibration regressions are not expected to be set through zero.

9.2.4.1 The linear regression curve is expressed as below:

$y = ax + b$

Where a is the slope and b is the y-intercept. When forced through 0, b=0.

$y = AS/ASUR$ $x = CS/CSUR$

AS is peak response of target analyte in calibration standards
ASUR is peak response of surrogate standard (SUR) in calibration standards
CS is concentration of target analyte in calibration standards
CSUR is concentration of surrogate standard (SUR) in calibration standards

9.2.5 Calibration Sequence

9.2.5.1 Calibration standards must be analyzed in sequence from lowest to highest concentration to minimize the chance that carryover from a higher concentration standard will boost the area of a lower concentration standard.

9.2.6 ICAL Evaluation

9.2.6.1 Acceptance Criteria – When quantitated using the ICAL curve, each calibration level for each analyte must calculate to be within 70-130% of its true value (±30% RE). For calibration curves produced using average response factors, the percent relative standard deviation (%RSD) of the RFs for all analytes must be <20%. Linear or non-linear regressions must have $r^2 \geq 0.99$ ($r \geq 0.995$) for each analyte. Weighting (typically 1/x or 1/x2) is allowed for linear and non-linear regressions. 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 ICAL standards, restrict the range of calibration, or select an alternate method of calibration.

9.2.6.1.1 Calibration Point Dropping – If more than the minimum number of standards are analyzed and levels are excluded from the calibration, only the lowest or highest standards may be excluded, except as noted here. The removal of calibration levels from the interior of the curve is allowed only when there is sound technical reason for doing so and when the level is removed for all analytes; for example, when it can be proven that the wrong standard was analyzed for the calibration level or there is obvious evidence that the instrument malfunctioned during injection of the standard. **The removal of any calibration level from the interior of the curve must be approved by the department supervisor/manager. Management approval and the rationale for the level removal must be documented and kept with the technical record.**

9.2.6.1.2 Calibration Point Replacement – replacing a calibration standard may sometimes be needed to correct for a technical problem that occurred during analysis such as power failure, incomplete injection of the standard or similar situation. Replacement of one standard, when analyzed within 24 hours of original analysis time and replacing all analytes in the original standard, is permitted. **The replacement of the standard must be approved by the department supervisor/manager; approval and the reason for replacement must be documented and kept with the technical record.**

9.2.6.1.3 For Wisconsin compliance analysis, re-quantitated concentrations for all target compounds at all concentration levels must be within the range 70-130% of their actual concentrations, except for the lowest calibration concentration level, which must be within the range of 50-150% of actual concentrations.

9.2.6.1.4 Calibration results for labeled Surrogate and Internal Standard compounds will be evaluated by comparing the area response of each level to the ICAL midpoint level (L5 – 1000ppt). Any ICAL points for which SUR or IS responses fall outside of 50-200% of the midpoint ICAL shall be removed. If any more than two ICAL points fail these criteria, the system should be inspected, and maintenance should be performed if needed. A new ICAL will then be analyzed following any maintenance.

NOTE: 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.

9.2.7 Calibration Locking – After all ICAL and ICV acceptance criteria are met, the calibration is considered “locked” and no further changes may be made until the next calibration event. In the AIM2 data processing software, the primary review (L1) analyst will set the “Sample State” for all files of the calibration event to “Locked” state. When files are in “Locked” state, no permanent changes can be made to the samples. The calibration design or fit must never be changed during routine data processing of any analytical sequence associated with the calibration; the only exception is when a problem with the original calibration curve is found. In that case, the problem must be handled as a quality incident. If the investigation of the incident indicates that the calibration is invalid, then all data associated with the calibration must be reprocessed under the corrected calibration.

9.2.8 Relative Error

9.2.8.1 Each calibration level for each analyte must calculate to be within 70-130% of its true value (±30% RE); except for Wisconsin compliance – see section 9.2.6.1.3.

9.2.9 Initial Calibration Verification (ICV)

9.2.9.1 As part of the IDOC, each time a new Analyte PDS is prepared, and once after each ICAL, analyze an ICV sample from a second source (different from the source of the ICAL 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, correct the problem and rerun the ICV. If the problem persists, repeat the ICAL. Samples are not to be analyzed until the ICAL has been verified by acceptable ICV accuracy. The lab will add additional target analytes to the ICV mix as second source standards become commercially available.

9.2.10 Continuing Calibration Verification/Instrument Sensitivity Check (CCV/ISC)

9.2.10.1 CCV Standards are analyzed at the beginning of each analysis batch, after every 10 samples, and at the end of the analysis batch. In this context, a “sample” is considered to be a field sample. MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs are not counted as samples. In the event that 10 field samples and various non-field sample QC (BLKs, MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs) are injected between a set of CCVs, the maximum injections between CCVs is limited to 20. Inject an aliquot of the appropriate concentration ICAL standard and analyze with the same conditions used during the initial calibration.

9.2.10.1.1 The daily Instrument Sensitivity Check (ISC; DOD required) will be used as the daily opening CCV and will be analyzed at a concentration at or below the LoQ using prepared ICAL standards.

9.2.10.1.2 The prepared mid-level ICAL solution will be analyzed for subsequent bracketing and closing CCVs.

9.2.10.1.3 Calculate the concentration of each analyte and surrogate in the CCV. The calculated amount for each analyte must be within ± 30% of the true value. The area response for each surrogate compound must be within ±50% of the area of the corresponding compound in the ICAL midpoint, or the ISC on days that an ICAL is not analyzed. If these conditions do not exist, then all data for the problem analyte must be considered invalid, and remedial action should be taken which may require recalibration. Any field or QC samples that have been 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 a particular method analyte, and the associated field sample extracts show no detection for that method analyte, non-detects may be reported with appropriate narrative, without the need for re-analysis.

9.2.10.1.3.1 For Wisconsin and other non-DoD compliance samples, the calculated amount for each analyte must be within ± 30% of the true value except for the ISC, for which the calculated amount of each analyte must be within ± 50% of the true value.

9.2.10.1.4 Remedial Action – Failure to meet CCV QC performance criteria may require remedial action. Major maintenance, such as cleaning the electrospray probe, cleaning the mass analyzer, replacing the LC column, etc., requires recalibration and verification of sensitivity by analyzing a CCV at or below the LOQ.

9.2.10.1.4.1 Remedial Actions taken to correct for ICAL, ICV, and CCV acceptance criteria exceptions must be documented and must be traceable to the ICAL/ICV/CCV for which the corrective action was performed. The instrument maintenance log entry for the remedial action must include some reference to the failing result (batch, ID, file number, etc) for which the remedial action is being taken.

9.2.10.1.5 If reanalysis cannot be performed, the data must be qualified. An NCM must be generated which describes the reason that reanalysis is not being performed.

9.3. Sample Preparation (Aqueous)

Some of the PFAS adsorb to surfaces, including polypropylene and HDPE. Therefore, aqueous sample containers must be rinsed with the elution solvent. The container rinse is passed through the cartridge to elute the method analytes and is then collected.

NOTE: The SPE cartridges, reservoirs, and sample containers described in this section are designed as single use items and should be discarded after use. They may not be refurbished for reuse in subsequent analyses.

9.3.1 Inspect samples; determine if sample centrifugation is warranted for each sample. Samples containing settled or suspended solids may require centrifugation in order to be fully loaded through the SPE sorbent; see Appendix C for more guidance in the Aqueous Sample Centrifugation Protocol. If centrifugation is warranted, follow the PFAS centrifuge procedure in Appendix C of this SOP.

9.3.1.1 Leachate samples and most samples from landfill-impacted sites will be prepared at an up-front (pre-extraction) dilution of 10X (25mL aliquot of sample into final volume of 250mL, using verified pipette).

9.3.2 Weigh the full sample container and document in LIMS3 prep batch. Initial volume for samples requiring centrifugation should be recorded after the centrifugation procedure has been completed.

9.3.3 Spike the sample containers with 100 µL of the 100 ppb SUR Mix. Invert the sample to mix.

9.3.4 Spike the LCS/LCSD, MS, and either FD or MSD appropriately according to the corresponding section under Quality Control and Method Performance (Section 11)

9.3.5 Clean SPE adapter caps by thoroughly rinsing with MeOH and allow to dry before using them to connect the cartridges/reservoirs.

9.3.6 Insert a disposable liner gently into the center of the flow valve. NOTE: tip of liner may catch and bend/break the liner. If that happens, try again with a new liner.

9.3.7 Attach the SPE extraction cartridges (Strata PFAS [WAX/GCB]) to the converter caps and the reservoirs. Place the cartridge setups in the active SPE manifold ports.

9.3.8 Wet the rim of the manifold body with DI water to form a proper seal with the manifold top.

9.3.9 Place the top on the SPE manifold, start the vacuum pump, and ensure the vacuum is approximately 5-10in. Hg.

9.3.10 Condition each SPE cartridge in individual steps with the following solvents. Solvent volumes used for conditioning step 1 should be used to rinse down the inside of the SPE reservoirs, to remove any potential contamination from the inside of the reservoirs. After adding the conditioning solvent to the reservoir/cartridge setup and before passing the solvent through the SPE sorbent for each conditioning step: in a *dropwise fashion*, the analyst must allow the conditioning solvent to soak the sorbent for 2 minutes, ensuring both sorbent beds (WAX and GCB) are fully soaked **(do not allow sorbent to go dry during conditioning).**

9.3.10.1 Conditioning step 1: 4mL Ammonia-MeOH (0.6%) + 4mL MeOH

9.3.10.2 Conditioning step 2: 4mL Ammonium acetate/acetic acid buffer

If the SPE cartridge goes dry during any step of the conditioning process, restart conditioning with first step (Amm-MeOH+MeOH).

9.3.11 Add the entire water sample to the SPE tube/reservoir **(do not allow sorbent to go dry during sample loading).**

9.3.11.1 Samples containing settled or suspended solids may require centrifugation in order to be fully loaded through the SPE sorbent; see Appendix C for the Aqueous Sample Centrifugation Protocol.

9.3.12 Adjust the pressure/SPE flow control valves to load the sample at approximately 10-15mL/min; this rate equates to loading time of 17-25 mins for a 250mL sample.

9.3.12.1 If the sample takes longer than 30 minutes to load through the SPE sorbent due to clogging, even after centrifugation, stop and continue with 9.3.13. A nonconformance memo must be used to document this.

9.3.13 Once the entire sample has passed through the SPE cartridge, wash the cartridge by passing 4 mL of the Ammonium Acetate/Acetic Acid buffer through the sorbent at a rate similar to the sample loading rate in 9.3.11

9.3.14 Use the vacuum to dry cartridges under high vacuum (≤20in. Hg) for ~5mins. Record drying start and end times.

9.3.15 Release the vacuum, remove the top from the SPE manifold and wet the rim of the manifold. Place the rack with the eluent collection tubes in the manifold and replace the top, ensuring that the active SPE ports are set in the corresponding collection tubes and a proper seal is formed. Turn the pump back on and ensure the pressure is approximately 5-10in. Hg.

9.3.16 Add 4mL MeOH to each empty sample container, then cap and shake each bottle to ensure all interior surfaces get rinsed. Transfer rinsate to the SPE, using a pipette to swirl MeOH along the insides of the reservoir to rinse.

9.3.17 Rinse each empty sample container a second time with 4mL Ammonia-MeOH (0.6 %). Transfer to the SPE, again using a pipette to swirl the Ammonia-MeOH solution along the inside of the reservoir to rinse.

9.3.18 Allow the eluent to soak the sorbent bed for 2 minutes before elution, as in 9.3.10. Collect the total eluent in the previously positioned collection tubes. Adjust the pressure/SPE flow control valves to elute in a ***slow*** dropwise fashion. Close each flow control valve just after the eluent level drops below the top frit of the cartridge – do not fully dry cartridges at this step.

9.3.19 Add 2mL MeOH to each cartridge, allowing the rinse solvent to soak the sorbent bed for 2 mins before eluting from the cartridge, as in 9.3.10.

NOTE: This soak may be visually different than previous soak steps in this protocol, as the entire volume of MeOH may fit in the body of the sorbent beds – there may not be any visible MeOH volume sitting on top of the sorbent bed.

9.3.20 Collect the entirety of the MeOH rinsate into the eluent collection tubes in a slow dropwise fashion, allowing the cartridges to fully dry. Release vacuum and remove collection tubes to a rack when elution is complete.

9.3.21 Weigh the empty container and document the weight in LIMS3 prep batch.

9.3.22 The difference between the weights from 9.3.2 and 9.3.21 is the sample volume (assuming 1g/mL density). Sample volumes will be rounded to the nearest 1.0 mL for use in calculations.

9.3.23 Using clean MeOH and individual Kimwipes, clean enough nozzles on the TurboVap LV concentrator to accommodate the number of sample extracts being concentrated. Make sure any nozzles not in use are firmly capped.

9.3.24 Concentrate extracts to an approximate volume of 4.0 mL (1.5mL if targeted final volume is 2 mL) using the TurboVap LV under a gentle stream of nitrogen in a heated water bath (55–60 °C). Set Nitrogen flow at a level which creates a vortex in the extract tube but does not cause splash-out; suggested starting flow rate is 1.5L/min.

9.3.25 Create a final volume (FV) reference tube: using a verified pipette, place a 5 mL or 2 mL aliquot of 96% MeOH into a clean extract tube – reference aliquot volume will depend on the targeted FV for the particular analysis selected

9.3.26 Once the sample extract has been concentrated to approximately 4.0 mL (1.5 mL if targeted final volume is 2 mL), remove elution tube from the TurboVap and allow to cool to room temperature.

9.3.27 Once cooled, reconstitute the extract following the appropriate row in the table below. After adding the water aliquot, use a transfer pipet and the reference tube created in 9.3.25 to bring the extract to the appropriate FV with clean reagent MeOH. Mix reconstituted extract to ensure homogeneity. Final reconstituted extract solvent composition is 96% MeOH: 4% water.

Extract targeted FV (mL)	Water (µL)
5	200
2	80

9.3.28 Transfer the reconstituted extracts to either 8mL HDPE Nalgene bottles or 2 mL cryovials, depending on extract FV, for storage at room temperature until instrumental analysis. Ensure caps are fully sealed on all extract storage bottles.

NOTE: For Wisconsin compliance samples, sample extracts must be stored at 0-6°C

9.3.29 Manifold cleanup – open flow control valves all the way and use the methanol squirt bottle to thoroughly rinse all flow control valves on the vacuum manifold top. Turn the manifold top on the side and rinse lures with methanol and flip the side and rinse the other side with methanol as well. Repeat the aforementioned steps with 0.6% ammonium methanol followed by methanol. If samples with high levels of contamination are processed, or if there is a concern that carryover contamination could impact samples yet to be prepared, Isopropyl Alcohol may be used to clean the manifold and flow control valves before the first methanol rinse.

9.3.30 For samples that show analyte detections above the range of the ICAL, sample dilutions will need to be prepared. See Appendix F for dilution preparation scheme.

9.3.30.1 Samples requiring analyses prepared at post-extraction dilutions of 50X or greater will be refortified with EIS to enable proper quantitation. Samples diluted in this manner are no longer technically quantitated using isotope dilution quantitation. All analyses prepared at post-extraction dilutions of 20X, 10X, or 5X will not be refortified with EIS and will thus maintain isotope dilution quantitation.

9.4. Analysis

9.4.1 Column Flush – Each day of analysis, the column must be thoroughly flushed with 100% MeOH for at least 30 minutes to clear any accumulated impurities and interferents from the sample pathway and equilibrate the system. It is also good practice to open the purge valve on the pumps for the first ~1min of flush time. The column should then be equilibrated to the analysis starting conditions by flushing for approximately 15 mins with 50:50 Ammonium Acetate: MeOH and finally approximately 15 mins with 95:5 Ammonium acetate: MeOH. Ensure that pressure is stable.

9.4.2 Analytical Sequence – Following the daily column flush, two to three (2-3) high ICAL standard (L9 or L10) injections and one blank injection will be made in order to prime the system before analyzing opening QC and client samples. Following these opening injections, Instrument Sensitivity Check (ISC) samples will be analyzed as the opening CCV (9.2.10). When a passing ISC sample(s) has been evaluated, an instrument blank will be analyzed to demonstrate the absence of system contamination. After system contamination is determined to be acceptable (no target analyte concentrations >1/2 LOQ), samples may be analyzed. After every tenth field sample analyzed in a sequence, a CCV will be analyzed (9.2.10), as well as at the end of the sequence. Each bracketing CCV should be followed by a CCB/IBLK sample injection. If system contamination is detected (any target analyte concentration >1/2 LOQ) in a CCB/IBLK following a bracketing CCV, and a Wisconsin compliance sample in the associated analysis window (prior to next CCV) shows a concurrent target analyte detection, that sample will be reanalyzed with an acceptable CCB. If the sample cannot be reanalyzed for some reason, the data for the CCB-detected compound(s) in the affected sample will be qualified with an NCM.

10.0 Data Analysis And Calculations

10.1 Qualitative Identification

10.1.1 Manual Integration

10.1.2.1 Manual changes to automated integration is called manual integration. Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are performed consistently and are ethically justified,

all manual integrations must be performed, reviewed, and recorded in accordance with corporate SOP ENV-SOP-CORQ-0006, Manual Integration.

10.2 Calculations

See the Laboratory Quality Assurance Manual [QAMP ME0012K] for equations for common calculations.

NOTE: The surrogate standard/Extracted Internal Standard (SUR/EIS) is used for quantitation in the PFAS ID methods.

10.2.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. Concentrations are calculated by measuring the product ions (Q3 Mass) listed in Table 4. Other ions may be selected at the discretion of the analyst.

10.2.2 Calculate analyte and surrogate concentrations using the multipoint calibration established in Section 9.2. Do not use daily calibration verification data to quantitate analytes in samples. Final analyte concentrations are adjusted to reflect the actual sample volume determined in Section 9.

Sample concentration for aqueous samples:

$$\text{Concentration (ng/L)} = (\text{Cs})(\text{DF})$$

Where:

DF = dilution factor
Cs – see below

From the equation in section 10.3.2, Cs is calculated as follows:

$$Cs = \left(\frac{As}{Asur} - b\right) \cdot \left(\frac{Csur}{a}\right)$$

Where:

As is peak response of target analyte in the sample
Asur is peak response of internal standard in the sample (SUR for isotope dilution methods)
Cs is concentration of target analyte in the sample
Csur is concentration of internal standard in the sample (SUR for isotope dilution methods)
a is the slope from the ICAL linear regression
b is the y-intercept from the ICAL linear regression

10.2.3 Results for target analytes must be quantified from the most recent ICAL analyzed on the same instrument. During both primary (L1) and secondary (L2) review, analysts must review the ICAL Form 6 RF report (ICAL summary) to ensure that the most recent ICAL analyzed on the same instrument was utilized for the quantitation of all samples.

10.3 Prior to reporting the data, the chromatogram must be reviewed by a trained analyst for any incorrect peak identification or poor integration.

10.4 Dilution - When the concentrations of target analytes on-column exceed the highest concentration of initial calibration standard, dilution analyses are required. An appropriate dilution should be in the upper half of the calibration range, or close to the CCV. The diluted extract must maintain the same methanol/water ratio as the original extract. If a dilution greater than 20X of the extract is required,

fortification of the SUR/EIS in the diluted extract is necessary. Samples requiring >20-fold diluted analyses post-extraction will be refortified with SUR/EIS to enable proper quantitation. Samples diluted in this manner are no longer technically quantitated using isotope dilution quantitation. Refer to Appendix F for dilution preparation information.

10.5 PFHxS, PFOS, MeFOSAA and EtFOSAA have multiple chromatographic peaks using the LC conditions in Table 4 due to the linear and branched isomers of these compounds. The areas of all the linear and branched isomer peaks observed in the ICAL standards for each of these analytes must be integrated together and summed. The concentrations are reported as a total for each of these analytes. Purchased standards contain both linear and branched isomers; therefore, individual ICALs for the linear and branched isomers will not be possible. PFOA also has multiple chromatographic peaks using the LC conditions in Table 4 due to linear and branched isomers of this compound. However, a quantitative standard containing both linear and branched isomers is not currently available, so ICAL standards will not show multiple peaks for PFOA. A technical (qualitative) standard is analyzed with each calibration event to identify where the branched isomer peak elutes, relative to the linear isomer peak. In client samples, the areas of the linear and branched isomer peaks observed must be integrated together and summed. The concentration of PFOA in client samples will be reported as a sum total of branched and linear isomers. As more standards (quantitative or qualitative) containing both branched and linear isomers for other target analytes become available, these will be used in the same way as for PFHxS/PFOS/MeFOSAA/EtFOSAA or PFOA. Following the same procedure, any target analyte for which a standard has been purchased and analyzed will be integrated and reported as a sum total of branched and linear isomers.

10.5.1 MeFOSAA and EtFOSAA standards containing branched and linear isomers are also present in the Isomer Check solutions.

10.6 Integration - Sample integration is performed automatically by quantitation software and reviewed by the analyst for any incorrect analyte identification or poor integration. A peak is considered a positive detection if the primary (quantitation) ion transition peak shows a signal-to-noise ratio (S/N) of at least 10.0:1 and is defined by at least 10 MS scans (data points) across the baseline of the peak. For analytes with a secondary (confirmation) ion transition, the primary and secondary ion transitions must elute at nominally the same retention time (±2 seconds). Further, the secondary transition must show S/N of at least 3.0:1.

10.6.1 For Wisconsin compliance and other analyses not regulated by the DoD, quantitation ion transition peaks are considered positive detections if the S/N is at least 3.0:1

10.6.2 Retention Time (RT) acceptance – RT of each analyte, SUR, and IS must fall within 0.4 minutes (±0.2 mins) of the corresponding RTs from the ICAL midpoint, or the daily ISC on days when ICAL is not performed. Analytes with matched (labeled analogue) SUR compounds must elute within 0.1 mins of the associated SUR.

10.7 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

10.8 Calculate the % recovery for the LCS using the following equation:

$$\%\ \text{Recovery} = \frac{\text{Concentration (or amount)found}}{\text{Concentration (or amount) spiked}} \times 100$$

10.9 Calculate the MS % recovery for each analyte using the equation:

$$\%\ \text{Recovery} = \frac{Xs - X}{t} \times 100$$

Where:
Xs = measured concentration in the spiked sample
X = measured concentration in the unspiked sample
t = spike concentration

10.10 Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2 or MS and MSD) using the equation:

$$\text{RPD} = \frac{|X2 - X1|}{\frac{X2 + X1}{2}} \times 100$$

Where:
X1 = FD1 or MS result
X2 = FD2 or MSD result

10.11 Calculate the percent relative standard deviation (%RSD) for calibration curves produced using average response factor using the equation:

$$\%\ \text{RSD} = \frac{SD}{AVG} \times 100$$

Where:
SD = the standard deviation of the curve
AVG = the average response factor for the curve (y = AVG*x)

10.12 Calculate the relative error (RE) using the equation:

$$\%RE = \frac{x_2 - x_1}{x_1} \text{ x } 100$$

Where:
X1 = true value of the calibration standard
X2 = measured concentration of the calibration standard

11.0 Quality Control And Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples.

QC Item	Frequency
Method Blank (MB)	1 per batch
Laboratory Control Sample (LCS)	1 per batch
Laboratory Control Sample Duplicate (LCSD)	As needed
Matrix Spike (MS)	1 per batch
Matrix Spike Duplicate (MSD)	1 per batch or as needed
Sample Duplicate	1 per batch or as needed

11.2 Instrument QC

The following Instrument QC checks are performed.

QC Item	Frequency
Initial Calibration (ICAL)	Following major instrument maintenance, when new ICAL standards are prepared, and as needed to account for instrumental drift
Instrument Blank (IBLK)	After calibration, daily prior to sample analysis, after each CCV
Initial Calibration Verification (ICV)	After calibration.
Continuing Calibration Verification (CCV)	At the beginning of each batch, after every 10 samples, and at end of each batch
Instrument Sensitivity Check (ISC)	Daily opening CCV(s)

11.3 Instrument Blank (IBLK) – One instrument blank (IBLK) is analyzed immediately following the highest ICAL standard analyzed, on a daily basis prior to sample analysis, and following each bracketing CCV in a sequence, to check for carryover and instrument contamination. The concentration of each analyte must be ≤ 1/2 the LOQ. If the instrument blank does not pass this requirement after the highest ICAL standard, the calibration must be performed using a lower concentration for the highest standard until the acceptance criteria is met.

11.3.1 If any target analyte is detected in both a Wisconsin compliance sample and the IBLK/CCB immediately preceding (following bracketing CCV), an NCM will be generated to document the potential bias. See 9.4.2.

11.4 Method Blank (MB) – One method blank (MB) must be processed with each extraction batch. If more than 20 samples are included in a batch, analyze an MB for every 20 samples. The MB is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis.

11.4.1 The MB must not contain any analyte of interest at or above 1/2 of the LOQ or project specific-requirements. (Note: see appendices for state or program specific requirements). If the MB contains an analyte of interest at or above 1/2 of the LOQ, then the MB and associated samples must be reanalyzed. If the MB contamination is confirmed, the entire batch must be re-prepared and reanalyzed. Reanalysis or re-extraction is not required if the samples are not impacted. Samples are not impacted when:

11.4.1.1 The MB detection is not present in the sample.

11.4.1.2 The sample concentration is ≥10x the concentration of the detection in the MB.

11.4.1.3 For any MB not associated with DOD-compliance samples OR Wisconsin-compliance samples, contamination must only be **≤LOQ** for each analyte. Other project-specific requirements may be used as well.

11.4.2 The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, sample analysis should stop immediately. Corrective action should be taken. The MB should be reanalyzed if the analyst feels that the failure could be attributed to instrument problems. If the analyst feels that the failure is due to a poor extraction, the entire batch associated with the MB must be re-extracted.

11.4.2.1 If a MB recovers above the acceptance limits for a SUR/EIS compound and is ND for the associated target compound in the MB AND associated samples show acceptable recovery for the same SUR/EIS compound, the MB is acceptable and sample data may be reported as is. If a sample associated with a MB showing a high-failing result for a SUR/EIS compound also shows recovery above the acceptance range but is ND for associated target compound(s), the data may be reported for that sample.

11.5 Laboratory Control Sample (LCS) – An LCS is required with each extraction batch. The spiked concentration of the LCS will be at a low concentration of the calibration curve. See DoD acceptance criteria for LCS targets in Table 6. If the LCS results do not meet the criteria listed in Table 6 for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. For target analytes not included in the DoD Limits for batch control table (Appendix C of QSM 5.3), in-house limits of 70-150% recovery will be used as acceptance criteria.

11.5.1 The LCS for ID-AQ is prepared by spiking 250 mL of reagent water with 200 µL of the 100X PDS mix (20 ppb) for a concentration of 16 ppt (GenX at 32 ppt). The LCS is also spiked with 100 µL of Full List 100 ppb SUR mix and extracted as normal alongside client samples.

11.5.2 For Wisconsin compliance and other non-DoD compliance samples, acceptance limits will be 50-150% recovery for all target compounds.

11.6 Surrogates (SUR/EIS/IDS) – The surrogate standard (SUR, also referred to as extracted internal standard [EIS] or isotope dilution standard [IDS]) is fortified into all samples, MBs, LCSs, MSs, MSDs prior to extraction. It is also included in the ICAL standards. SUR/EIS indicate extraction efficiency in sample prep and are used to quantitate target analytes in all samples.

11.6.1 The analyst must monitor the peak areas of the SUR in all injections during each analysis day. The SUR responses (peak areas) in any chromatographic run must not deviate by more than 50% from the area measured in the ICAL midpoint (L5) standard during initial calibration or in the daily opening CCV on days a calibration is not performed. When the SUR/EIS/IDS recovery from a sample, blank, or CCV is not within this range check the following: calculations to locate possible errors, standard solutions for degradation or contamination, and instrument performance. Correct the problem and inject a second preparation of that sample extract (or blank or CCV) prepared in a new capped autosampler vial. Loss due to evaporation has been observed when using polypropylene caps which can cause high SUR response.

11.6.2 For Wisconsin and other non-DoD compliance analysis, all SUR/EIS/IDS compounds must recover within the range 25-150% in extracted samples, except 13C8-PFOSA, d3-MeFOSA, d5-EtFOSA, d7-MeFOSE, and d9-EtFOSE, which must recover within the range 10-150% in extracted samples. Recovery will be based on area counts as described above. For all instrument QC (CCV, ICV, ICB, CCB, IBLK) used for Wisconsin compliance, SUR/EIS/IDS compounds must recover within the range 50-150% in each injection.

11.6.3 If extract reanalysis meets the surrogate recovery acceptance criteria, report only the data for the reanalyzed extract.

11.6.4 If the extract reanalysis fails the 50-150% acceptance criteria (or 10/25-150% for non-DoD compliance), the analyst should check the calibration by injecting the last ICAL standard that passed. If the ICAL standard fails the criteria of 9.2.6, maintenance and/or recalibration is in order. If the ICAL standard is acceptable, extraction of the sample should be repeated provided the sample is still within the holding time. If the re-extracted sample also fails the recovery acceptance criteria, an NCM will be generated describing that the results are suspect due to surrogate recovery. Alternatively, a new sample can be collected and re-analyzed.

11.7 Ion Ratios – In detections of analytes for which two ion transitions (quantitation and confirmation) are measured, the area ratio between the confirmation and quantitation transitions shall be monitored and documented. The ion ratio for all detected analytes in each injection should be within 50-150% of the average ion ratio for the same analyte in the ICAL. On days ICAL is not performed, the ion ratio should be within 50-150% of the initial CCV standard. Targets detected and identified with ion ratios that fail these acceptance criteria will be flagged in the quantitation report, but not disqualified.

11.8 Matrix Spike (MS) – Analysis of an MS is required in each extraction batch. Assessment of method precision can be accomplished by analysis of a duplicate collected in the field; however, infrequent occurrence of method analytes might hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a matrix spike duplicate (MSD) must be prepared, extracted, and analyzed. Extraction batches that contain MSD will not require the extraction of an FD.

11.8.1 Within each extraction batch, a minimum of one sample is spiked as an MS for every 20 samples analyzed. Client samples are spiked in the same manner as the LCS. 250mL of sample is spiked with 200 µL of 100X PDS mix (20 ppb) plus 100 µL of Full List 100 ppb SUR mix and extracted as normal alongside other client samples.

11.8.1.1 Analyte recoveries may exhibit matrix effect. For matrix spike samples, recoveries should range between 70-150%. If the % recovery falls outside of the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the LCS. If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. Analytical reports will show qualifier flags in such cases.

11.8.1.2 If the recovery for any analyte is outside the acceptance criteria for the matrix spike and the LCS, the laboratory is out of control and corrective action will be taken. Corrective action may include re-preparation and reanalysis of the batch. An NCM will be generated to document the corrective action taken.

11.9 Field Duplicate (FD) or Matrix Spike Duplicate (MSD) – Within each extraction batch (not to exceed 20 Field Samples), a minimum of one FD or MSD must be analyzed. If method analytes are not routinely observed in field samples, an MSD should be analyzed rather than an FD. See Appendix G for MS/MSD, MS/FD sample selection guidance.

11.9.1 Relative Percent Differences (RPDs) – FDs should have RPDs that are ≤30% between the original sample and the FD. If the RPD of any analyte falls outside the acceptance criteria, and the laboratory performance for that analyte is shown to be in control in the LCS, the recovery is judged to be matrix biased.

11.9.2 RPDs for MS/MSDs should be ≤30%. If the RPD falls outside of the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the LCS. If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. Analytical reports will show qualifier flags in such cases.

11.9.3 Every effort is made to ensure that an MS/MSD or an FD is included in every batch. In the event that there is insufficient sample to analyze an MS/MSD pair or if no FD is available, a duplicate LCS (laboratory control sample duplicate (LCSD)) is included in the batch. The MS/MSD must be analyzed at the same dilution as the most concentrated reportable analysis of the parent sample (the un-spiked sample See Appendix G for MS/MSD, MS/FD sample selection guidance.

11.10 Trip Blank (TB) – The purpose of the TB is to ensure that PFAS measured in the samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the TB is required only if a sample contains a method analyte or analytes at or above the LOQ; by lab protocol, TB samples are prepared and analyzed when received, prior to any knowledge of associated sample contamination. The TB is processed, extracted and analyzed in exactly the same manner as the samples. If an analyte found in the sample is present in the TB at a concentration greater than 1/2 the LOQ, then all samples collected with that TB are invalid and must be recollected and reanalyzed.

11.11 Reagent Water Contamination Testing – in-house generated reagent water demonstrated to be reasonably free of PFAS compounds, will be used for QC samples (MB/LCS/LCSD) in extraction batches and also sent to clients for use as trip blanks (TB), field blanks (FB), and equipment blanks (EB). Tested reagent water may also be sent to client sampling sites for other uses. Reagent water used for these purposes will be tested by the lab to confirm the absence of PFAS compounds prior to shipping to clients or being used in the lab. Carboys routinely will be filled with reagent water from the in-house Milli-Q water filtration system in order to create in-house “lots” of water; a sample bottle will be prepared each time carboys are filled and tested as a MB (contamination check) and LCS (spike recovery check) using the ID-AQ method. The test samples will be logged into the LIMS system by the PFAS supervisor or a member of QA when a set of carboys are filled to create a new in-house lot. The physical test samples shall be created by sampling approximately equal amounts of water from each filled carboy, which together constitute the “lot” of water. These test samples will be treated exactly the same as all other client and QC samples, taken through the entire extraction and analysis process. Should there be any recovery issues or any PFAS contamination detected in the reagent water collected in a particular lot, the water in that lot will not be used further for PFAS QC or field use. The lot may be tested again to confirm the recovery issue and/or the presence of contamination. If long-term outage of the in-house reagent water system occurs, reagent water may be purchased from an approved vendor; when new lots

of reagent water are received from the vendor, one sample from one of the bottles of the new lot will be tested in the same manner as described above. Reagent water lots and testing results will be recorded in document ME0047N-01: PFAS Free Reagent Water Milli Q System Water Testing; naming convention for in-house generated water lots will follow the convention of PFAS-YY-###, in which "YY" is the last two digits of the current year and "###" is a three digit number indicating the sequential lot number (ex: PFAS-21-005 is the 5th lot generated in 2021).

11.12 Method Performance

11.12.1 Method Validation

11.12.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification and to the *Method Validation* SOP [QA Policy ME003BF] for these procedures.

11.12.1.2 The MDL spike samples were prepared by spiking 250 mL of reagent water with 50 µL of 1000X PDS mix (2ppb), for a concentration of 0.4 ng/L (ppt; 50 ppt on column), plus 100 µL of Full List 100ppb SUR mix and extracted as normal. Final extract was concentrated/reconstituted to a final volume of 2 mL. An equal number of MB (see section 11.4) were extracted and analyzed with MDL samples.

11.12.1.3 MRL samples for Wisconsin compliance analysis will be spiked at twice the target analyte concentration of the MDL spiked samples.

11.12.1.4 Routine, on-going MDLv samples will be prepared by spiking 250 mL of reagent water with 25 µL of 100X PDS mix (20ppb), for a concentration of 2 ng/L (ppt; 100 ppt on column), plus 100 uL of Full List 100ppb SUR mix and extracted as normal. Final extract will be concentrated/reconstituted to a final volume of 5 mL. These samples will be prepared and analyzed at least twice per quarter.

11.12.1.5 For non-standard, non-regulatory analytes, an MDL study should be performed, and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client.

11.13 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to the *Demonstration of Capability* SOP [QA SOP ME001F2] for more information.

12.0 Data Review and Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and

properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employees complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to the *Data Review* SOP [QA SOP ME003LP] for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range. Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detections of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration (L5) indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 Pollution Prevention And Waste Management

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 Modifications

14.1 A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP

ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1.1 The analyst is permitted to modify LC columns, LC conditions, internal standards or surrogate standards, and MS and MS/MS conditions. Each time such method modifications are made, the analyst must repeat the procedures of the IDOC. **Modifications to LC conditions should still produce conditions such that co-elution of the method analytes is minimized to reduce the probability of suppression/enhancement effects.**

15.0 Responsibilities

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 Attachments

16.1 Appendix A: Tables

16.1.1 Table 1 – Target Analyte List

16.1.2 Table 2 – Reporting Limits (LOQ)

16.1.3 Table 3 – Labeled Standard Associations

16.1.4 Table 4 – Instrument Conditions

16.1.5 Table 5 – Calibration Levels

16.1.6 Table 6 – DoD Batch Control Limits

16.2 Appendix B – PFAS ID – Solid Matrix

16.3 Appendix C – Aqueous Sample Centrifugation Protocol

16.4 Appendix D – PFAS by TCLP/SPLP

16.5 Appendix E - Aqueous Serial Dilution

16.6 Appendix F – Extract Dilution Preparations

16.7 Appendix G – MS/MSD, MS/FD Sample Selection Guide

16.8 Appendix H – Chemical Derivation of Ion Transitions

16.9 Appendix I – DoD/DOE QSM Requirements

17.0 References

NOTE: Where references exclude a date or edition, the latest edition of the referenced document adopted/recognized by the laboratory's accreditation bodies applies. Refer to the Quality Assurance Management Plan [QAMP ME0012K] for details.

17.1 *Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography* / Tandem Mass Spectrometry (LC/MS/MS), USEPA, Method 537.1, Version 1.0, November 2018.

17.2 *Department of Defense Department of Energy Consolidated Quality Systems Manual (QSM)* for Environmental Laboratories

17.3 Water Quality – Determination of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) – Method for Unfiltered Samples Using Solid Phase Extraction and Liquid Chromatography/Mass Spectrometry, ISO 25101:2009 €.

17.4 Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) detection, USEPA, SW846, Method 9321B, Revision 2, February 2007.

17.5 Knepper, T.P. (2003) Analysis and Fate of Surfactants in the Aquatic Environment. Amsterdam, The Netherlands; Elsevier Science B.V.

17.6 Knepper, T.P. (2012) Polyfluorinated Chemicals and Transformation Products. Berlin, Germany: Springer-Verlag Berlin Heidelberg.

17.7 Rapid Commun Mass Spectrom 2007;21 (23): 3803-14.

17.8 *Wisconsin Department of Natural Resources Notice of Final Guidance and Certification, Wisonsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations*. Wisconsin DNR. Version 12.16.2019.

18.0 Revision History

Revision #	Section Modified	Modification	Reason for Modification
v04	Appendix C	Removed Chip Method	Created separate SWI
	Appendix D	Removed Bottle Rinsate Method	Created separate SWI

APPENDIX A: TABLES

TABLE 1 – TARGET ANALYTE LIST

Analyte Name	Analyte Acronym	CAS Number	Method 537.1	ID (Aqueous)	DAI	ID (Solid)
1H,1H,2H,2H-perfluorohexane sulfonic acid	4:2 FTS	757124-72-4*	No	Yes	No	Yes
1H,1H,2H,2H-perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	No	Yes	No	Yes
1H,1H,2H,2H-perfluorodecane sulfonic acid	8:2 FTS	39108-34-4	No	Yes	No	Yes
1H,1H,2H,2H-perfluorododecane sulfonic acid	10:2FTS	120226-60-0*	No	Yes	No	Yes
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6	Yes	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9	Yes	Yes	No	Yes
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5*	Yes	Yes	Yes	Yes
Perfluoro-n-butanoic acid	PFBA	375-22-4	No	Yes	Yes	Yes
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3*	No	Yes	No	Yes
Perfluoro-n-decanoic acid	PFDA	335-76-2	Yes	Yes	Yes	Yes
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	Yes	Yes	No	Yes
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8*	Yes	Yes	No	Yes
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	Yes	Yes	Yes	Yes
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4*	Yes	Yes	Yes	Yes
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Yes	Yes	Yes	Yes
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1*	Yes	Yes	No	Yes
Perfluoro-n-nonanoic acid	PFNA	375-95-1	Yes	Yes	Yes	Yes
Perfluorooctanesulfonic acid	PFOS	1763-23-1*	Yes	Yes	Yes	Yes
Perfluoro-1-octanesulfonamide	PFOSA	754-91-6	No	Yes	No	Yes
Perfluoro-n-octanoic acid	PFOA	335-67-1	No	Yes	Yes	Yes
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	Yes	Yes	Yes	Yes
Perfluoro-1-pentansulfonic acid	PFPeS	2706-91-4*	Yes	Yes	No	Yes
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	Yes	Yes	No	Yes

TABLE 1 – TARGET ANALYTE LIST (CONT'D)

Analyte Name	Analyte Acronym	CAS Number	Method 537.1	ID (Aqueous)	DAI	ID (Solid)
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	Yes	Yes	No	Yes
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8	Yes	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamide	MeFOSA	31506-32-8	No	Yes	No	Yes
N-ethylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2	No	Yes	No	Yes
Hexafluoropropylene oxide dimer acid	GenX	13252-13-6	Yes	Yes	No	Yes
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	Yes	Yes	No	Yes
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1*	Yes	Yes	No	Yes
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUDS	763051-92-9*	Yes	Yes	No	Yes
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	MeFOSE	24448-09-7	No	Yes	No	Yes
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	EtFOSE	1691-99-2	No	Yes	No	Yes
Perfluoro-1-dodecanesulfonic acid	PFDOS	79780-39-5*	No	Yes^	No	Yes^
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	No	Yes^	No	Yes^
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	No	Yes^	No	Yes^

* CAS Numbers are for the acid and not the salt.
^ Compounds for Wisconsin compliance analysis
NOTE: Methods 537.1 and DAI are addressed in SOPs ME002I6 and ME002I7 respectively.

TABLE 2A – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – AQUEOUS MATRIX

NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (ng/L)	DL (ng/L)	LOD (ng/L)	LOQ (ng/L)
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	2991-50-6	0.4	1	4	8
8:2 FTS	1H,1H,2H,2H-perfluorodecane sulfonic acid	39108-34-4	0.383	1	4	8
4:2 FTS	1H,1H,2H,2H-perfluorohexane sulfonic acid	757124-72-4[2]	0.374	1	4	8
6:2 FTS	1H,1H,2H,2H-perfluorooctane sulfonic acid	27619-97-2	0.379	1	4	8
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	2355-31-9	0.4	1	4	8
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5[2]	0.354	0.5	2	4
PFBA	Perfluoro-n-butanoic acid	375-22-4	0.4	0.5	2	4
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3[2]	0.386	0.5	2	4
PFDA	Perfluoro-n-decanoic acid	335-76-2	0.4	0.5	2	4
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	0.4	0.5	2	4
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8[2]	0.381	0.5	2	4
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.4	0.5	2	4
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4[2]	0.364	0.5	2	4
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	0.4	0.5	2	4
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1[2]	0.384	0.75	2	4
PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.4	0.5	2	4
PFOS	Perfluorooctanesulfonic acid	1763-23-1[2]	0.371	0.5	2	4
PFOSA	Perfluoro-1-octanesulfonamide	754-91-6	0.4	0.75	2	4

TABLE 2A – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – AQUEOUS MATRIX CONT'D
NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (ng/L)	DL (ng/L)	LOD (ng/L)	LOQ (ng/L)
PFOA	Perfluoro-n-octanoic acid	335-67-1	0.4	0.5	2	4
PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	0.4	0.5	2	4
PFPeS	Perfluoro-1-pentansulfonic acid	2706-91-4[2]	0.375	0.5	2	4
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	0.4	0.5	2	4
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	0.4	0.5	2	4
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	0.4	0.5	2	4
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	0.4	2	8	16
EtFOSA	N-ethylperfluoro-1-octanesulfonamide	4151-50-2	0.4	1.5	4	8
10:2FTS	1H,1H,2H,2H-perfluorododecane sulfonic acid	120226-60-0[2]	0.386	1	4	8
GenX	Hexafluoropropylene oxide dimer acid	13252-13-6	0.8	1	4	8
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	0.377	1	4	8
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1[2]	0.373	1	4	8
11Cl-PF3OUDS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9[2]	0.377	1	4	8
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	0.4	1	4	8
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	0.4	1	4	8
PFDOS	Perfluoro-1-dodecanesulfonic acid	79780-39-5[2]	0.387	1	4	8
PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5	0.4	1	4	8
PFODA	Perfluoro-n-octadecanoic acid	16517-11-6	0.4	1	4	8

[1]Spiking concentration used to determine DL.
[2]CAS Numbers are for the acid and not the salt.

TABLE 2B – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – SOLID MATRIX
NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (µg/kg)	DL (µg/kg)	LOD (µg/kg)	LOQ (µg/kg)
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	2991-50-6	0.1	0.25	1	2
8:2 FTS	Fluorotelomer sulfonate 8:2 [1H,1H,2H,2H-perfluorodecane sulfonate]	39108-34-4	0.096	0.25	1	2
4:2 FTS	Fluorotelomer sulfonate 4:2 [1H,1H,2H,2H-perfluorohexane sulfonate]	757124-72-4[2]	0.093	0.4	1	2
6:2 FTS	Fluorotelomer sulfonate 6:2 [1H,1H,2H,2H-perfluorooctane sulfonate]	27619-97-2	0.095	0.25	1	2
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	2355-31-9	0.1	0.25	1	2
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5	0.088	0.13	0.5	1
PFBA	Perfluoro-n-butanoic acid	375-22-4	0.1	0.13	0.5	1
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3	0.096	0.13	0.5	1
PFDA	Perfluoro-n-decanoic acid	335-76-2	0.1	0.13	0.5	1
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	0.1	0.13	0.5	1
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8	0.095	0.13	0.5	1
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.1	0.13	0.5	1
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4	0.091	0.13	0.5	1
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	0.1	0.13	0.5	1
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1	0.096	0.2	0.5	1
PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.1	0.13	0.5	1
PFOS	Perfluorooctanesulfonic acid	1763-23-1	0.093	0.13	0.5	1
PFOSA	Perfluoro-1-octanesulfonamide	754-91-6	0.1	0.13	0.5	1

TABLE 2B – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – SOLID MATRIX CONT'D
NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (µg/kg)	DL (µg/kg)	LOD (µg/kg)	LOQ (µg/kg)
PFOA	Perfluoro-n-octanoic acid	335-67-1	0.1	0.13	0.5	1
PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	0.1	0.13	0.5	1
PFPeS	Perfluoro-1-pentanesulfonic acid	2706-91-4	0.094	0.13	0.5	1
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	0.1	0.13	0.5	1
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	0.1	0.13	0.5	1
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	0.1	0.13	0.5	1
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	0.1	0.25	1	2
EtFOSA	N-ethylperfluoro-1-octanesulfonamide	4151-50-2	0.1	0.4	1	2
10:2FTS	1H,1H,2H,2H-perfluorododecane sulfonate	120226-60-0[2]	0.096	0.25	1	2
GenX	Tetrafluoro-2-(heptafluoropropoxy) propanoic acid	13252-13-6	0.2	0.5	2	4
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	0.094	0.25	1	2
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1	0.093	0.25	1	2
11Cl-PF3OUDS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	0.094	0.25	1	2
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	0.1	0.25	1	2
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	0.1	0.25	1	2
PFDOS	Perfluoro-1-dodecanesulfonic acid	79780-39-5[2]	0.097	0.13	0.5	1
PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5	0.1	0.25	1	2
PFODA	Perfluoro-n-octadecanoic acid	16517-11-6	0.1	0.13	0.5	1

[1]Spiking concentration used to determine DL.
[2]CAS Numbers are for the acid and not the salt.

TABLE 3 – LABELED STANDARD ASSOCIATIONS – PFAS ISOTOPE DILUTION – AQUEOUS AND SOLID MATRIX

Target Analyte	Associated Labeled Standard
4:2 FTS	13C2_4:2FTS_2
6:2 FTS	13C2_6:2FTS_2
8:2 FTS	13C2_8:2FTS_2
10:2FTS	13C2_8:2 FTS_2
EtFOSAA	d5-EtFOSAA
MeFOSAA	d3-MeFoSAA
PFBS	13C3_PFBS
PFBA	13C4_PFBA
PFDS	13C8_PFOS
PFDA	13C6_PFDA
PFDoA	13C2_PFDoA
PFHpS	13C3_PFHxS
PFHpA	13C4_PFHpA
PFHxS	13C3_PFHxS
PFHxA	13C5_PFHxA
PFNS	13C8_PFOS
PFNA	13C9_PFNA
PFOS	13C8_PFOS
PFOSA	13C8_PFOSA
PFOA	13C8_PFOA
PFPeA	13C5_PFPeA
PFPeS	13C3_PFBS
PFTeDA	13C2_PFTeDA
PFTrDA	13C2_PFDoA
PFUdA	13C7_PFUdA
MeFOSA	d3-MeFOSA
EtFOSA	d5-EtFOSA
GenX	13C3-GenX
ADONA	13C3_PFHxS
9Cl-PF3ONS	13C8_PFOS
11Cl-PF3OUDS	13C8_PFOS
MeFOSE	d7-MeFOSE
EtFOSE	d9-EtFOSE
PFDOS	13C8_PFOS
PFHxDA	13C2-PFHxDA
PFODA	13C2-PFHxDA

NOTE: For method ID-AQ and ID-Solid, the labeled quantitation standards are contained in the SUR solution.

TABLE 4: ID INSTRUMENT CONDITIONS – AQUEOUS AND SOLID MATRIX

LC Program

Step	Total Time (min)	Flow Rate (uL/min)	A: 20mM Ammonium Acetate (%)	B: Methanol (%)
0	0.00	1200	95.0	5.0
1	0.10	1200	45.0	55.0
2	4.50	1200	1.0	99.0
3	6.00	1200	1.0	99.0
4	6.10	1200	95.0	5.0
5	8.10	1200	95.0	5.0

Built-in Diverter Valve Program

Step	Total Time (min)	Position
1	0.0	Waste
2	1.0	MS
3	5.8	Waste

Instrument Parameters

Parameter	Setting or Value
Syringe Size	100 µL
Injection Volume	10 µL
Draw Speed	50.0 µL/min
Eject Speed	50.0 µL/min
Needle Level	3.0 mm
Column Oven Temperature	40°C
MRM Scan Window	30 sec
Curtain Gas (CUR)	30.0
Collision Gas (CAD)	9
Ion Spray Voltage (IS)	-4500.0 V
Temperature (TEM)	450.0°C
Ion Source Gas 1 (GS1)	40.0
Ion Source Gas 2 (GS2)	60.0

MS/MS Conditions*

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
4:2 FTS	327	307	2.42	-20	-4	-28	-8
4:2 FTS_2	327	81	2.42	-20	-4	-50	-8
6:2 FTS	427	407	3.23	-20	-4	-32	-8
6:2 FTS_2	427	81	3.23	-20	-4	-72	-8
8:2 FTS	527	507	4.02	-20	-4	-40	-8
8:2 FTS_2	527	81	4.02	-20	-4	-82	-8
9Cl-PF3ONS	531	351	3.88	-75	-10	-38	-10
10:2 FTS	627	607	4.66	-20	-8	-45	-8
10:2 FTS_2	627	80	4.66	-20	-8	-92	-8
11Cl-PF3OUDS	631	451	4.52	-90	-10	-41	-13
ADONA	377	251	2.95	-47	-8	-18	-8
ADONA_2	377	85	2.95	-47	-8	-68	-8
EtFOSA	526	169	4.71	-50	-10	-37	-8
EtFOSA_2	526	219	4.71	-50	-10	-37	-8
EtFOSE	630	59	4.65	-39	-4	-58	-8
GenX	285	119	2.58	-51	-10	-38	-8
GenX_2	285	185	2.58	-51	-10	-28	-8
MeFOSA	512	169	4.52	-50	-10	-37	-8
MeFOSA_2	512	219	4.52	-50	-10	-37	-8
MeFOSE	616	59	4.49	-50	-10	-58	-8
N-EtFOSAA	584	419	4.36	-50	-10	-28	-8
N-EtFOSAA_2	584	526	4.36	-50	-10	-28	-8
N-MeFOSAA	570	419	4.20	-50	-10	-28	-8
N-MeFOSAA_2	570	483	4.20	-50	-10	-22	-8
PFBA	212.9	168.9	1.71	-10	-8	-12	-8
PFBS	298.9	80	2.15	-20	-4	-56	-5.5
PFBS_2	298.9	99	2.15	-20	-4	-46	-9
PFDA	513	469	4.03	-10	-8	-17	-8
PFDA_2	513	169	4.03	-10	-8	-27	-8
PFDoA	613	569	4.66	-10	-8	-18	-8
PFDoA_2	613	169	4.66	-10	-8	-30	-8
PFDOS	699	80	4.65	-150	-10	-125	-7
PFDOS_2	699	99	4.65	-150	-10	-120	-10
PFDS	599	80	4.34	-20	-7	-118	-5.5
PFDS_2	599	99	4.34	-20	-7	-95	-9
PFHpA	363	319	2.85	-10	-8	-14	-8
PFHpA_2	363	169	2.85	-10	-8	-25	-8
PFHpS	449	80	3.27	-20	-4	-80	-5.5
PFHpS_2	449	99	3.27	-20	-4	-70	-9
PFHxA	313	269	2.46	-10	-8	-14	-8
PFHxA_2	313	119	2.46	-10	-8	-25	-8
PFHxDA	813	769	5.31	-123	-13	-22	-19

MS/MS Conditions Continued*

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
PFHxDA_2	813	269	5.31	-123	-6.5	-37	-22
PFHxS	399	80	2.87	-20	-4	-74	-5.5
PFHxS_2	399	99	2.87	-20	-4	-60	-9
PFNA	463	419	3.66	-10	-8	-16	-8
PFNA_2	463	169	3.66	-10	-8	-26	-8
PFNS	549	80	4.02	-20	-5.5	-115	-5.5
PFNS_2	549	99	4.02	-20	-5.5	-92	-5.5
PFOA	413	369	3.26	-10	-8	-14	-8
PFOA_2	413	169	3.26	-10	-8	-26	-8
PFODA	913	869	5.70	-120	-9	-25	-15
PFODA_2	913	319	5.70	-120	-9	-42	-15
PFOS	499	80	3.66	-20	-4	-95	-5.5
PFOS_2	499	99	3.66	-20	-4	-87	-9
PFOSA	498	78	4.02	-20	-4	-85	-8
PFPeA	262.9	218.9	2.09	-10	-8	-13	-8
PFPeS	349	80	2.50	-20	-4	-70	-5.5
PFPeS_2	349	99	2.50	-20	-4	-60	-9
PFTeDA	713	669	5.15	-10	-4	-22	-8
PFTeDA_2	713	169	5.15	-10	-4	-38	-8
PFTrDA	663	619	4.92	-10	-4	-20	-8
PFTrDA_2	663	169	4.92	-10	-4	-36	-8
PFUdA	563	519	4.36	-10	-8	-18	-8
PFUdA_2	563	169	4.36	-10	-8	-28	-8
13C2-PFDA	515	470	4.03	-10	-8	-17	-8
13C2-PFDoA	615	570	4.66	-10	-4	-18	-8
13C2-PFHxA	315	270	2.46	-10	-8	-14	-8
13C2-PFHxDA	815	770	5.31	-107	-10	-24	-16
13C2-PFOA	415	370	3.26	-10	-8	-14	-8
13C2-PFTeDA	715	670	5.15	-10	-4	-22	-8
13C3-GenX	287	185	2.58	-55	-10	-24	-10
13C3-PFBA	216	172	1.71	-10	-8	-12	-8
13C3_PFBS	302	80	2.15	-20	-4	-56	-5.5
13C3_PFHxS	402	80	2.87	-20	-4	-74	-5.5
13C4_PFBA	217	172	1.71	-10	-8	-12	-8
13C4_PFHpA	367	322	2.85	-10	-8	-14	-8
13C4_PFOS	503	80	3.66	-20	-4	-95	-5.5
13C5_PFHxA	318	273	2.46	-10	-8	-14	-8
13C5_PFPeA	267.9	223	2.09	-10	-8	-13	-8
13C6_PFDA	519	474	4.03	-10	-8	-16	-8
13C7_PFUdA	570	525	4.36	-10	-8	-18	-8

MS/MS Conditions Continued*

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
13C8_PFOA	421	376	3.26	-10	-8	-14	-8
13C8_PFOS	507	80	3.66	-20	-4	-95	-5.5
13C8_PFOSA	506	78	4.02	-20	-4	-85	-8
13C9_PFNA	472	427	3.66	-10	-8	-16	-8
d3-MeFOSA	515	169	4.52	-50	-10	-37	-8
d3-MeFOSAA	573	419	4.20	-50	-10	-28	-8
d5-EtFOSA	531	169	4.71	-50	-10	-37	-8
d5-EtFOSAA	589	419	4.36	-50	-10	-28	-8
d7-MeFOSE	623	59	4.49	-50	-5.5	-58	-5.5
d9-EtFOSE	639	59	4.65	-60	-4	-60	-8
M2-4:2 FTS	329	309	2.42	-20	-4	-28	-8
13C2-4:2 FTS_2	329	81	2.42	-20	-4	-28	-8
M2-6:2FTS	429	409	3.23	-20	-4	-32	-8
13C2-6:2FTS_2	429	81	3.23	-20	-4	-32	-8
M2-8:2FTS	529	509	4.02	-20	-4	-40	-8
13C2-8:2FTS_2	529	81	4.02	-20	-4	-82	-8

*Some MS/MS conditions may need to be re-optimized for individual instruments

NOTE: See Appendix I for the chemical derivation of the ion transitions.

TABLE 5: CALIBRATION LEVELS (ng/L) – ID ICAL – AQUEOUS AND SOLID MATRIX

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9	Level 10
	PFAS Full List Native PDS Mix, 1000X			PFAS Full List Native PDS Mix, 100X			PFAS Full List Native PDS Mix, 10X			
PFBA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFPeA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFBS	44	88	177	442	884	1768	4420	8840	13260	17680
PFHxA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFPeS	47	94	188	469	938	1876	4690	9380	14070	18760
PFHpA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFHxS	46	91	182	455	910	1820	4550	9100	13650	18200
PFOA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFHpS	48	95	190	476	952	1904	4760	9520	14280	19040
PFNA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFOS	46	93	186	464	928	1856	4640	9280	13920	18560
PFDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFNS	48	96	192	480	960	1920	4800	9600	14400	19200
4:2FTS	47	93	187	467	934	1868	4670	9340	14010	18680
6:2FTS	47	95	190	474	948	1896	4740	9480	14220	18960
8:2 FTS	48	96	192	479	958	1916	4790	9580	14370	19160
PFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000

TABLE 5: CALIBRATION LEVELS (ng/L) – ID ICAL – AQUEOUS AND SOLID MATRIX CONT'D

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9	Level 10
	PFAS Full List Native PDS Mix, 1000X			PFAS Full List Native PDS Mix, 100X			PFAS Full List Native PDS Mix, 10X			
MeFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFUDA	50	100	200	500	1000	2000	5000	10000	15000	20000
MeFOSAA	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSAA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFDS	48	96	193	482	964	1928	4820	9640	14460	19280
PFDoA	50	100	200	500	1000	2000	5000	10000	15000	20000
10:2FTS	48	96	193	482	964	1928	4820	9640	14460	19280
PFTrDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFTeDA	50	100	200	500	1000	2000	5000	10000	15000	20000
GenX	100	200	400	1000	2000	4000	10000	20000	30000	40000
ADONA	47	94	188	471	942	1884	4710	9420	14130	18840
9Cl-PF3ONS	47	93	186	466	932	1864	4660	9320	13980	18640
11Cl-PF3OUDS	47	94	188	471	942	1884	4710	9420	14130	18840
MeFOSE	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSE	50	100	200	500	1000	2000	5000	10000	15000	20000
PFDOS	48	97	194	484	968	1936	4840	9680	14520	19360
PFHxDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFODA	50	100	200	500	1000	2000	5000	10000	15000	20000
Surrogates (SUR)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000

NOTE: See Table 1 for method specific target analytes.

NOTE: *The ID (Aqueous and Solid) SUR includes the following compounds:*

- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] hexane sulfonate (M2-4:2FTS or 13C2-4:2FTS)
- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] octane sulfonate (M2-6:2FTS or 13C2-6:2FTS)
- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] decane sulfonate (M2-8:2FTS or 13C2-8:2FTS)
- Perfluoro-1-[13C8] octanesulfonamide (M8FOSA-I or 13C8FOSA)
- N-ethyl-d5-perfluoro-1-octanesulfonamide (d-N-EtFOSA-M)

- N-methyl-d3-perfluoro-1-octanesulfonamide (d-N-MeFOSA-M)
- N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA)
- N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA)
- Perfluoro-n-[13C4]butanoic acid (MPFBA or 13C4PFBA)
- Perfluoro-n-[13C5]pentanoic acid (M5PFPeA or 13C5PFPeA)
- Perfluoro-n-[1,2,3,4,6-13C5]hexanoic acid (M5PFHxA or 13C5PFHxA)
- Perfluoro-n-[1,2,3,4-13C4]heptanoic acid (M4PFHpA or 13C4PFHpA)
- Perfluoro-n-[13C8]octanoic acid (M8PFOA or 13C8PFOA)
- Perfluoro-n-[13C9]nonanoic acid (M9PFNA or 13C9PFNA)
- Perfluoro-n-[1,2,3,4,5,6-13C5]decanoicanoic acid (M6PFDA or 13C6PFDA)
- Sodium perfluoro-1-[2,3,4-13C3]butanesulfonate (M3PFBS or 13C3PFBS)
- Sodium perfluoro-1-[1,2,3-13C3]hexanesulfonate (M3PFHxS or 13C3PFHxS)
- Sodium perfluoro-1-[13C8]octanesulfonate (M8PFOS or 13C8PFOS)
- Perfluoro-n-[1,2,3,4,5,6,7-13C7]undecanoic acid (M7PFUdA or 13C7PFUdA)
- Perfluoro-n-[1,2-13C2]dodecanoic acid (MPFDoA or 13C2PFDoA)
- Perfluoro-n-[1,2-13C2]tetradecanoic acid (M2PFTeDA or 13C2PFTeDA)
- Tetrafluoro-2-(heptafluoropropoxy)-13C3 propanoic acid (13C3-GenX)
- 2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)
- 2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)
- Perfluoro-n-[1,2-$^{13}C_2$] hexadecanoic acid (13C2-PFHxDA)

TABLE 6A: DOD BATCH CONTROL LIMITS – AQUEOUS MATRIX*

The limits outlined in this table shall be used when reporting data for DoD/DOE projects

CAS	Analyte Acronym	Lower Control Limit (%REC)	Upper Control Limit (%REC)
2991-50-6	EtFOSAA	61	135
39108-34-4	8:2 FTS	67	138
757124-72-4	4:2 FTS	63	143
27619-97-2	6:2 FTS	64	140
2355-31-9	MeFOSAA	65	136
375-73-5	PFBS	72	130
375-22-4	PFBA	73	129
335-77-3	PFDS	53	142
335-76-2	PFDA	71	129
307-55-1	PFDoA	72	134
375-92-8	PFHpS	69	134
375-85-9	PFHpA	72	130
355-46-4	PFHxS	68	131
307-24-4	PFHxA	72	129
68259-12-1	PFNS	69	127
375-95-1	PFNA	69	130
1763-23-1	PFOS	65	140
754-91-6	PFOSA	67	137
335-67-1	PFOA	71	133
2706-90-3	PFPeA	72	129
2706-91-4	PFPeS	71	127
376-06-7	PFTeDA	71	132
72629-94-8	PFTrDA	65	144
2058-94-8	PFUdA	69	133
31506-32-8	MeFOSA	68	141
4151-50-2	EtFOSA	70	150
120226-60-0	10:2FTS	70	150
13252-13-6	GenX	70	150
919005-14-4	ADONA	70	150
756426-58-1	9Cl-PF3ONS	70	150
763051-92-9	11Cl-PF3OUDS	70	150
24448-09-7	MeFOSE	70	150
1691-99-2	EtFOSE	70	150

***For Wisconsin compliance analysis, LCS recovery limits for all compounds are 60-135% when spiked at mid-range or high-range concentrations; 50-150% when spiked at low-range concentration.**

TABLE 6B: DOD BATCH CONTROL LIMITS – SOLID MATRIX*

The limits outlined in this table shall be used when reporting data for DoD/DOE projects

CAS	Analyte Acronym	Lower Control Limit (%REC)	Upper Control Limit (%REC)
2991-50-6	EtFOSAA	61	139
39108-34-4	8:2 FTS	65	137
757124-72-4	4:2 FTS	62	145
27619-97-2	6:2 FTS	64	140
2355-31-9	MeFOSAA	63	144
375-73-5	PFBS	72	128
375-22-4	PFBA	71	135
335-77-3	PFDS	59	134
335-76-2	PFDA	69	133
307-55-1	PFDoA	69	135
375-92-8	PFHpS	70	132
375-85-9	PFHpA	71	131
355-46-4	PFHxS	67	130
307-24-4	PFHxA	70	132
68259-12-1	PFNS	69	125
375-95-1	PFNA	72	129
1763-23-1	PFOS	68	136
754-91-6	PFOSA	67	137
335-67-1	PFOA	69	133
2706-90-3	PFPeA	69	132
2706-91-4	PFPeS	73	123
376-06-7	PFTeDA	69	133
72629-94-8	PFTrDA	66	139
2058-94-8	PFUdA	64	136
31506-32-8	MeFOSA	70	150
4151-50-2	EtFOSA	70	150
120226-60-0	10:2FTS	70	150
13252-13-6	GenX	70	150
919005-14-4	ADONA	70	150
756426-58-1	9Cl-PF3ONS	70	150
763051-92-9	11Cl-PF3OUDS	70	150
24448-09-7	MeFOSE	70	150
1691-99-2	EtFOSE	70	150

***For Wisconsin compliance analysis, LCS recovery limits for all compounds are 60-135% when spiked at mid-range or high-range concentrations; 50-150% when spiked at low-range concentration.**

APPENDIX B. PFAS ID – SOLID MATRIX

1. Standard Preparation

NOTE: Refer to the main body of this SOP for information regarding reagents and standards not listed here, specifically section 8.2 through 8.3

1.1 Solid Spiking Standard (SSS) – For ID-Solid, a separate solution of target analytes will be prepared and used to spike all QC samples (LCS, MS/MSD) used for 3M-TSM regulated analyses prior to extraction. The nominal concentration of all target analytes will be 500 ng/mL, except GenX which will be 1000 ng/mL. The SSS is stable for 12 months when stored at 2-6°C and contains 96% MeOH:4% Water. Prepare according to the table below:

ID Solid Spiking Standard (SSS)

Component	Conc. of Stock Std.	Aliquot volume	Dilution Volume	Final Conc.
	ng/mL	µL	mL	ng/mL
PFAC-30PAR	1000	2000	4	500
MeFOSA	50000	40	4	500
EtFOSA	50000	40	4	500
10:2 FTS	48200	40	4	482
GenX	50000	40	4	500
MeFOSE	50000	40	4	500
EtFOSE	50000	40	4	500
PFDOS	50000	40	4	484
PFHxDA	50000	40	4	500
PFODA	50000	40	4	500

1.2 Method Blank (MB) – Weigh 1.0g of Ottawa sand into a pre-tared 15mL Falcon tube and spike with 100µL of 100ppb SUR mix. Extract as normal alongside client samples.

1.3 Continuing Calibration Verification/Instrument Sensitivity Check (CCV/ISC) – See Section 9.2.10 in the main body of this SOP.

1.4 Laboratory Control Sample (LCS) – The LCS is prepared by spiking approximately 1g of Ottawa sand with 100 µL of 100X PDS (20 ng/mL) for a concentration of 2 µg/kg (2000 pg/g; 2000 ng/kg; 2 ng/g). The LCS is also spiked with 100 µL of Full List SUR mix (100 ppb) and extracted as normal alongside client samples.

1.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Client samples are spiked in the same manner as an LCS. 1g of sample is spiked with 100 µL of 100X PDS (20 ng/mL) for a concentration of 2 µg/kg, plus 100µL of Full List SUR mix (100ppb) and extracted as normal alongside other client samples.

1.6 Method Detection Limit (MDL) – MDL sample preparation and analysis will be performed over three separate days. Each MDL sample will be extracted with an equal number of MB samples. The MDL is prepared by spiking approximately 1g of Ottawa sand with 50 µL of 100X PDS mix for a concentration of 1000 pg/g (1000 ng/kg; 1 µg/kg), plus 100µL of Full List SUR mix (100ppb) and extracted as normal. An equal number of MB (see section 1.16 above) will be extracted and analyzed with MDL samples.

1.7 Initial (and Continuing) Demonstration of Capability (IDOC/CDOC) – The IDOC/CDOC is prepared by spiking approximately 1g of Ottawa sand with 100 µL 100X PDS plus 100µL of Full List SUR mix (100ppb) and extracted as normal. IDOC/CDOC sample final concentration equals 2µg/kg. Four replicates should be prepared and analyzed.

1.8 Ammonia-Methanol (Amm-MeOH, 0.6%) – In a 1000 mL graduated cylinder, add 20 mL NH4OH (Ammonium Hydroxide) and fill to volume with methanol (980 mL reagent MeOH). Invert to mix.

2. Sample Preparation

2.1 Allow samples time to come to room temperature.

2.2 Homogenize sample with a tongue depressor and/or vigorously shake sample container to ensure sample homogeneity.

2.3 Weigh approximately 1.0 g of sample into a pre-labeled, pre-tared 15 mL Falcon tube, record sample weight.

2.4 Spike sample aliquot with 100 µL 100ppb SUR mix; spike QC samples appropriately with PDS

2.5 Add 4 mL MeOH and 4 mL 0.6% Amm-MeOH to sample tube and cap tightly.

2.6 Place sample tubes on orbital shaker table for 30-35mins, on level 9.

2.7 Place samples in a tray and place the tray in a sonic bath at room temperature, sonicate for 30-35mins.

2.8 Remove rack from sonic bath and dry individual sample tubes before placing in a centrifuge and centrifuge at 3000RPM for 5 mins.

2.9 If centrifugation of sample does not fully separate solids from the extraction fluids, the resultant supernatant can be decanted from original sample tube into a clean centrifuge tube by pouring or using a plastic pipette. Decanting the supernatant from poorly separated extracts may help speed up the filtration process.

2.10 Place 25mg GCB pass-through cartridges, with pre-labeled reservoirs attached, into individual active luer ports in the vacuum manifold top.

2.11 Wet rim of manifold body and place manifold top on manifold body. Start the vacuum pump and ensure that a proper seal is formed between the manifold top and body, and vacuum is at a proper level (approximately 5-10 in. Hg).

2.12 Condition the GCB cartridges by passing 3mL MeOH in a slow drop-wise fashion through the tube, allowing the conditioning solvent to fully soak the sorbent for 2 mins before passing through the cartridge. Discard eluent. Do not dry GCB cartridges; if a cartridge goes dry, restart the conditioning step.

2.13 Release vacuum and remove manifold top. Place a rack containing clean, labelled 15mL Falcon tubes in the manifold body and replace the top. Ensure that the correct luer is inserted into the corresponding falcon tube in the manifold body.

2.14 Start vacuum and ensure proper seal and vacuum are achieved.

2.15 Load decanted extracts into corresponding labelled reservoirs and begin passing the extracts through the GCB cartridges in a drop-wise fashion; collect in the previously positioned clean, labelled 15mL Falcon tubes.

2.16 When the entire extract has eluted through the tube, close the stopcock to keep the tube from drying before/during the following step.

2.17 Rinse each tube with 2mL of clean MeOH, allowing the rinse solvent to fully soak the sorbent for 2 mins before passing through the cartridge (as in 2.12 above), and collect the rinsate in a slow drop-wise fashion.

2.18 Release vacuum, remove manifold top from body, and remove collection tubes. Cap tubes and invert to mix.

2.19 Concentrate extracts to an approximate volume of 4.0 mL (1.5mL if targeted final volume is 2 mL) using the TurboVap LV under a gentle stream of nitrogen in a heated water bath (55–60 °C). Set Nitrogen flow at a level which creates a vortex in the extract tube, but does not cause splash-out; suggested starting flow rate is 1.5L/min

2.20 Create a final volume (FV) reference tube: using a verified pipette, place a 5 mL or 2 mL aliquot of 96% MeOH into a clean extract tube – reference aliquot volume will depend on the targeted FV for the particular analysis selected

2.21 Once the sample extract has been concentrated to approximately 4.0 mL (1.5mL if targeted final volume is 2 mL), remove elution tube from the TurboVap and allow to cool to room temperature.

2.22 Once cooled, reconstitute the extract following the appropriate row in the table below. After adding the water aliquot, use a transfer pipet and the reference tube created in 2.20 to bring the extract to the appropriate FV with clean reagent MeOH. Vortex reconstituted extract to ensure homogeneity. Final reconstituted extract solvent composition is 96% MeOH: 4% water.

Extract targeted FV (mL)	Water (µL)
5	200
2	80

2.23 Transfer the reconstituted extracts to either 2 mL cryovials or 8mL HDPE Nalgene bottles, depending on extract FV, for storage at room temperature until instrumental analysis. Avoid transferring any remaining settled solids in the reconstituted extracts. Ensure caps are fully sealed on all extract storage bottles.

2.24 Manifold cleanup – see section 9.3.29 in main body of SOP

2.25 For samples that show analyte detections above the range of the ICAL, sample dilutions will need to be prepared. See Appendix G for dilution preparation scheme

2.25.1 Samples requiring analyses prepared at post-extraction dilutions of 50X or greater will be refortified with EIS to enable proper quantitation. Samples diluted in this manner are no longer technically quantitated using isotope dilution quantitation. All analyses prepared at post-extraction dilutions of 20X, 10X, or 5X will not be refortified with EIS and will thus maintain isotope dilution quantitation

APPENDIX C: AQUEOUS SAMPLE CENTRIFUGATION PROTOCOL

Preliminary considerations – The DoD QSM5.3, Table B-15, states that "[aqueous] samples with >1% solids may require centrifugation prior to SPE extraction." Additionally, the Wisconsin Department of Natural Resources (WDNR) guidance document, titled "Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations," states "add the EIS [Extracted Internal Standard] before any extraction, centrifuging, filtering or phase separation takes place…Samples should only be centrifuged when the suspended solids content appears visually high enough, by chemist inspection, that it would cause the SPE cartridge to clog…It is expected that the solid phase remains in the container when rinsing the container walls with the polar elution solvent. Rinsing the container walls would therefore also include rinsing of the solids. If removing the solvent disrupts the solid phase significantly, the container can be centrifuged again before removing the solvent for use during the elution step of the SPE procedure…When the sample has significant solids, the laboratory should account for the weight or volume displaced by the solids in the initial sample volume determination…One or more rinses of polar solvent can be used for quantitative transfers. Rinse the sample bottle and cap with elution solvent, pour the solvent from each rinse through the SPE cartridge during the elution step, and collect the filtrate for analysis. Bring to a quantitative final volume with the final injection solvent and vortex well." Whether or not an individual sample will require centrifugation for proper preparation will be determined and documented by the preparation analyst.

Procedure:

1.1 Inspect the sample and consider the necessity of centrifuging. Consider any visible indications of particulate matter including settled solids collected on the bottom of the container, cloudiness and/or dark color of the sample, suspended solids within the sample, increased viscosity, etc. If uncertain, seek a second opinion from another analyst, supervisor, or operations director.

1.2 If, in the judgement of the preparation analyst, a sample requires centrifugation the analyst will contemporaneously make a note on the prep batch log indicating this fact.

1.3 Spike samples requiring centrifugation in the same manner and with the same standard volume as samples which will not be centrifuged.

1.4 Label a 500mL conical centrifuge bottle with the sample ID for each sample that will be centrifuged. Set them in an appropriate rack with the caps removed.

1.5 Vigorously shake the spiked sample and then quickly pour into the labeled centrifuge bottle. Try to ensure that the original sample bottle is devoid of any solid material. Be careful to avoid spilling sample during the transfer process. Tightly cap each centrifuge bottle after transfers are complete.

1.6 Transfer capped centrifuge bottles to centrifuge, ensuring that the centrifuge carousel is symmetrically balanced. Close top and centrifuge at 3000 RPM for 6 minutes.

1.7 Remove centrifuge bottles and decant the centrifuged liquid off of the condensed solids, back into the original sample bottle. Try to avoid transferring any of the condensed solids from the centrifuge

bottle back to the original sample bottle, while maximizing the amount of liquid decanted off of the solid portion.

1.8 Weigh the full, decanted original sample bottle and document in the LIMS prep batch.

1.9 Extract the decanted sample as normal alongside un-centrifuged samples, up to the bottle rinse and elution steps.

1.10 When the SPE cartridges have been dried, rinse the original sample bottle as normal. Additionally, add 4mL of Methanol (MeOH) to each centrifuge bottle to rinse the inside of the centrifuge bottles as well as the cap. If the condensed solids become re-suspended while rinsing the centrifuge bottles, re-centrifugation may be required. Using a transfer pipet or mechanical pipet, transfer the MeOH rinse from the centrifuge bottle into the SPE cartridge and elute with the original sample bottle rinse into a 15mL conical centrifuge tube.

Note: If any samples in a prep batch have been centrifuged, all sample extracts in the batch should be eluted into 15mL conical centrifuge tubes, as the standard centrifuge tubes typically used to collect the eluent are shorter than the 15mL conical tubes. This may cause loss of extract during elution due to the tips of the male luers on the underside of the manifold not actually being located within the top of the shorter (standard) centrifuge tubes during elution.

1.11 Add an additional volume of MeOH to the elution of all batch QC samples (MB/LCS/LCSD) to match the volume used for elution for any centrifuged sample in the prep batch. Typically, this will mean that 4mL of clean MeOH will be added directly to the SPE reservoir and eluted with the normal bottle rinses.

Batch QC and client samples with additional container rinse volume should be filtered as normal.

1.12 After elution, all sample extracts (client and QC) shall be concentrated and reconstituted following the protocols in sections 9.3.22 through 9.3.27 in the main body of this SOP. Determine initial sample volume using the weights measured in 2.8 and the protocols in sections 9.3.20 and 9.3.21 in the main body of this SOP.

1.13 Generate a Non-Conformance Memo (NCM) noting which samples in the prep batch included centrifugation in the extraction process and any additional observations and/or deficiencies that were noted during the centrifugation process.

APPENDIX D: PFAS by TCLP/SPLP

SUMMARY

Clients may submit samples (solid or aqueous) for PFAS by TCLP or SPLP analyses. For solid samples, the TCLP and SPLP procedures are used to simulate the leaching of environmental contaminants over extended periods of time from a solid material into the environment. A subsample of the client's solid sample is weighed out and combined with a leaching solution and mechanically tumbled for a set period of time. Each leachate prep method (TCLP or SPLP) employs a unique leaching solution dictated by the TCLP and SPLP parent methods. After the sample has been tumbled/leached by the Extractions department, the leachate is filtered by the Inorganic Metals department and delivered to the PFAS sample holding area. The PFAS department is notified by email when the leachate solutions are ready for PFAS prep. Aqueous samples are not tumbled in the way that solid samples are prepared, but are simply filtered by the same method in the Inorganic Metals department. The filtered leachate solutions are prepared by the PFAS prep analysts using the ID-AQ SPE prep method, at a 1:10 dilution (1 part leachate solution, 9 parts reagent water).

PROCEDURE

Prep:

1. Samples requested for PFAS by SPLP/TCLP analysis will batched and leached by the normal SPLP/TCLP procedures used by the Extractions department (EXT). EXT will be the initial responsible party for samples analyzed for PFAS by SPLP/TCLP.
2. When the leaching process is complete, EXT will collect approximately 250mL (at minimum 100mL) of the leachate solutions in clean HDPE containers provided by the PFAS department.
3. After collecting the leachate solution, EXT will deliver the collected leachates to the Inorganic Metals department (IM) and verbally notify an IM prep team member. EXT will typically also send an email to the PFAS group to notify that the leaching process is complete.
4. An IM analyst will filter at least 100mL of each leachate solution using a Flipmate apparatus, using normal protocols for Flipmate filtration.
5. After filtering the leachates, the IM analyst will deliver the filtrates to the PFAS sample holding area (INM walk-in cooler) and send an email to the PFAS group to notify that the filtrates are ready for PFAS SPE prep.
6. Samples to be analyzed for PFAS by TCLP/SPLP will appear on a separate PFAS prep worklist (widget), the title of which will contain "SPLP" or "TCLP" (three separate lists so far, depending on leaching method and program area). PFAS analysts will select from these lists the samples to be extracted.
7. Using a verified variable pipet, transfer 25mL of filtrate solution to a pre-labeled HDPE PFAS sample bottle. Using pre-tested reagent water, fill the sample bottle to approximately 250mL. Each TCLP/SPLP filtrate sample will be prepared at a 10X dilution, using 25mL of the leachate filtrate, brought to a final volume of ~250mL using reagent water. Initial volume will be recorded as 25mL for all samples. As a result, LOQs for PFAS by TCLP/SPLP will be 10X higher than normal ID-AQ LOQs.
8. Following the instructions in step 7, use the leachate blank solution (typically has sample ID XX00000-038) to prepare two bottles for use as batch QC. Volume for the leachate blank and LCS will be recorded as 25mL, matching all samples.
9. Label and fill a clean 250mL HDPE bottle with ~250mL of pre-tested reagent water for use as a typical PFAS MB sample. Volume for the PFAS MB will be recorded as 250mL.

10. After preparing the diluted filtrate, filtrate batch QC, and PFAS MB bottles, follow the normal extraction steps for ID-AQ analysis. Each sample will be spiked with EIS standard as normal. The filtrate LCS will be spiked with target analytes according to the ID-AQ protocol for LCS target spiking.
11. Leachate batch QC (MB/LCS) should be documented in LIMS3 as a leachate blank (LEB) and as an LCS; the reagent water blank should be documented as the MB.

Analysis:

12. After PFAS SPE prep has been completed, the instrumental analyst will analyze the extracts by the full list ID-AQ method, as normal.
13. Before processing ***solid*** SPLP/TCLP samples in the AIM data processing software, the “Matrix” field in the Sample Editor app must be changed to “Aqueous”.
14. After processing, reviewing, and generating reports for the data, import the data into LIMS4. Before performing final calculations on the imported sample data in LIMS4, the values in the “InitialVolume” and “InitialWeight” columns must be made to match. For all but the PFAS MB, this will mean copying the 25 from “InitialWeight” to “InitialVolume;” for the PFAS MB, this will mean copying the 250 from “InitialVolume” to “InitialWeight.”
15. Once the changes in step 14 have been affected, calculate final results, then L1 and upload.

APPENDIX E. AQUEOUS SERIAL DILUTION

1 Standard Preparation

1.1 IS, SUR, and ICV standard solutions prepared for ID-AQ are used for samples analyzed by serial dilution instead of SPE. See Section 8 in the main body of the SOP for more information on preparation and contents of these solutions.

1.2 Dilutions of individual analyte stock standards are used for fortifying post-spike samples. Typically, these diluted stocks are prepared by a two-step serial dilution for a nominal concentration of 5ppb (some analytes have different concentrations due to differing stock concentrations). These diluted stocks are prepared by diluting 10uL of stock solution with 950uL of MeOH and 40uL of reagent water (FV=1mL), then further diluting 10uL of this initial 100X solution with 990uL of 96% MeOH, for a final dilution of 10,000X. The 10,000X DIL stock solution will typically be used for fortifying post-spike samples.

1.3 ICALs, ICAL standards, and instrument QC (CCVs, IBLKs) are the same as for ID-AQ and all acceptance criteria used for ID-AQ applies.

1.4 Samples analyzed by serial dilution do not require an LCS or MB to be prepared alongside the samples, as no extraction is performed. Daily IBLKs take the place of MBs.

2 Sample Preparation – Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE, with documented project approval.

2.1 All solutions prepared for instrumental analysis in this section and Section 3 shall have a solvent composition of 96:4% MeOH:water.

2.2 An initial dilution of the sample is made up with no IS or SUR added, to be used as the base dilution for successive serial dilutions. This initial dilution is typically prepared at 100X.

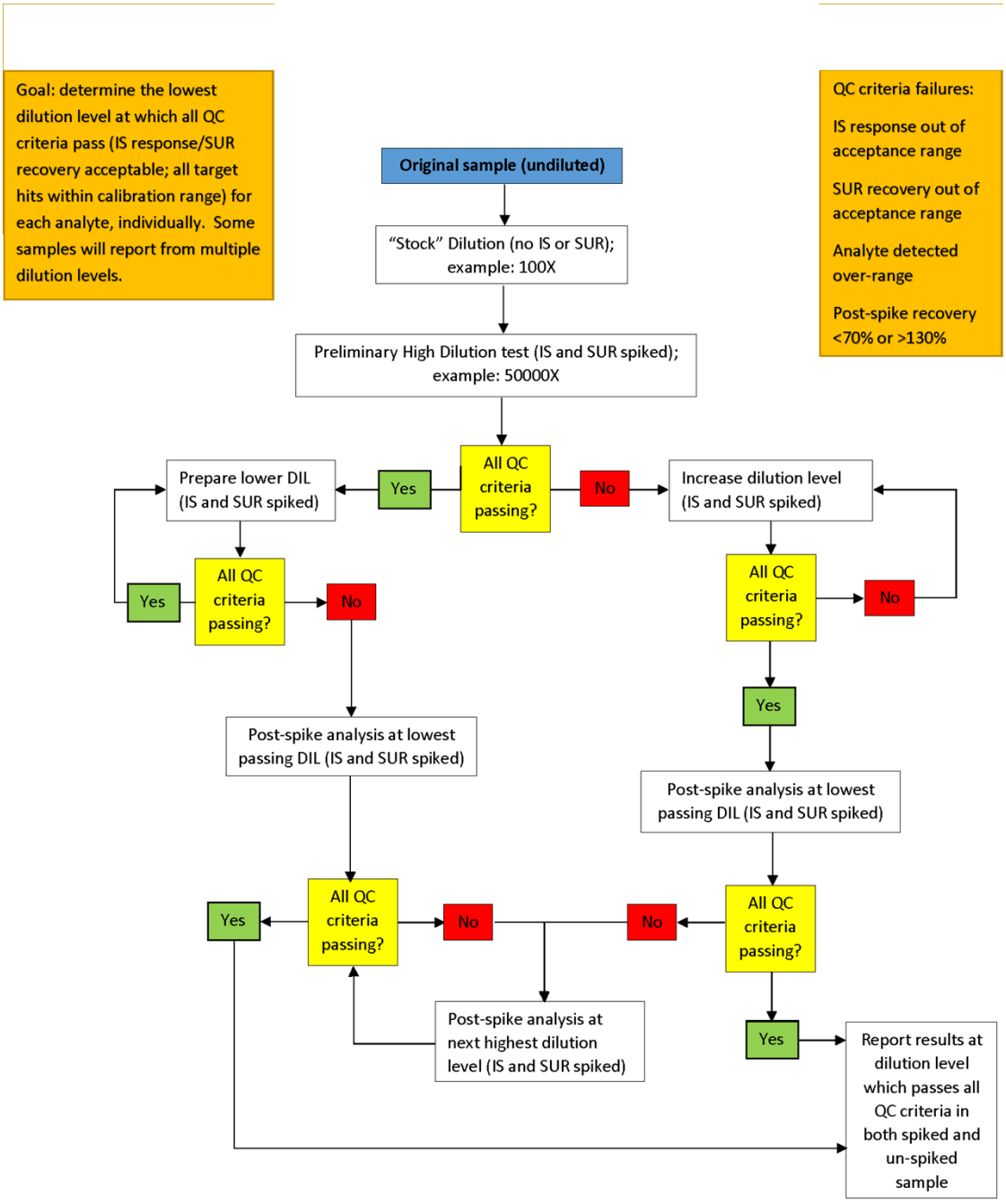
2.3 Using the initial sample dilution, prepare a high dilution (e.g. 50,000X) and analyze it to determine the approximate concentration of target analytes in the samples. Use the information obtained from this analysis to determine the next serial dilution to be prepared. Be sure to include IS and SUR standards at the appropriate concentration in each analyzed serial dilution. IS/SUR compounds should typically be present at a concentration of 1000pg/mL (1ppb).

2.4 Prepare successively lower dilutions of each serial dilution sample until all target analytes fail for over-range detection, IS response being out of acceptance, and/or SUR recovery being out of acceptance. Use the Non-Extracted Method PFAS Serial Dilution Prep Log and Post-spike Log (ME002DR) to record dilution and post-spike preparations. Be sure to include IS and SUR standards at the appropriate concentration in each analyzed serial dilution. No serial dilution samples will be analyzed at a dilution below 25X, in order to maintain proper solvent composition in the analyzed sample.

NOTE: Each target analyte should be evaluated individually in each serial dilution preparation. Associated IS/SUR compounds must pass acceptance criteria for an individual analyte to be reported. If the associated SUR and/or IS for one compound fails in a dilution sample, but *any* others pass, further dilution analysis will be necessary. Once a dilution level is reached in which all targets fail for one of the above-stated reasons, analysis will begin on the post-spiked samples.

2.5 For each target analyte, determine the dilution level at which the sample fails for one of the reasons stated in Section 2.4. The corresponding post-spike sample should be prepared at the next highest dilution level; in other words, determine the lowest dilution level at which a target analyte and its corresponding IS/SUR pass and prepare post-spike samples beginning at that dilution level.

Serial Dilution Decision Tree



3 **Post-spike sample preparation –** Post-spike samples must be prepared for all serial dilution samples which are ND for any target analyte at the reported dilution level. Non-detected target analytes will be individually spiked into post-spike dilution preparations at an expected on-column concentration equal to the stated LOQ in order to validate the stated LOQ in the sample matrix. If an analyte is detected in

a reportable dilution, no post-spiking of that analyte is required; the LOQ will equal the stated LOQ times the dilution factor of the reported analysis.

3.1 Post-spike samples must be prepared at the same dilution level as the reported sample results, and spiked at a concentration equivalent to the LOQ in the diluted sample. Post-spike analysis shall be prepared and evaluated for EACH non-detected analyte in EACH sample.

3.2 Calculate the appropriate amount of 10000X DIL stock solution necessary for the post-spike preparation by using the following equation:

$$\text{Spike Volume (mL)} = \frac{\text{LOQ(pg/mL)} * \text{final volume(mL)}}{\text{DIL stock(pg/mL)}}$$

3.3 Calculate the appropriate amount of 20ppb SUR and 20ppb IS necessary for the post-spike preparation by using the following equation:

$$\text{Spike Volume (mL)} = \frac{\text{1000(pg/mL)} * \text{final volume(mL)}}{\text{20000(pg/mL)}}$$

3.4 Prepare post-spikes at the reported dilution level for all ND analytes and record all post-spike preparation information using ME002DR. Use this logbook to ensure final volumes are correct and that all post-spike samples have solvent concentrations of 96% MeOH.

3.4.1 The analyte post-spiked into the dilution preparation must recover within 70-130% in order to be acceptable/reportable. All other QC criteria must be met as well (IS, SUR passing; opening/closing CCVs passing; acceptable IBLK).

3.4.2 Only the target analyte(s) being spiked and its corresponding IS/SUR must pass for each individual post-spike sample to be acceptable.

3.4.3 If a spiked analyte does not meet the 70-130% recovery limit, re-prepare the post-spike sample at successively higher dilutions using the steps above until recovery is within acceptance limits and corresponding IS/SUR compounds pass.

3.5 When a post-spike sample passes recovery and other QC criteria for the specific analyte(s) spiked, post-spiking analysis is complete for that sample/analyte combination.

3.6 The dilution reported for any individual analyte shall be the same dilution at which the post-spike sample passes for that analyte. If the initial post-spike sample fails when prepared at the expected reportable sample dilution, the LOQ has not been validated for this dilution level. Therefore, the reported dilution for that analyte/sample will be elevated to match the lowest passing dilution level of the post-spike analysis.

Report analyte results from the lowest dilution level which passes for all sample and post-spike QC criteria. The LOQ for ND analytes will equal the stated LOQ times the reported dilution factor.

APPENDIX F. EXTRACT DILUTION PREPARATIONS

Pace Analytical	Document Name: Extraction Dilution Preparations	Document Revised: 3/21/2022 Page 1 of 1
	Document No.: ME003.IZ-04	Issuing Authority: Pace ENV – Local Quality - WCOL

Extract Dilution Preparations

DILUTION	1X	5X	10X	20X	50X	100X	200X
537.1 DILUTION PREP							
EXTRACT (µL)	ALIQUOT	200	100	50	20	10	5
IS (µL)	0	40	45	47.5	49	49.5	49.75
96% MeOH (µL)	0	760	855	902.5	931	940.5	945.25
TOTAL (µL)	75	1000	1000	1000	1000	1000	1000
REFORTIFIED ID-AQ/ID-SOLID DILUTION PREP							
EXTRACT (µL)	ALIQUOT	200	100	50	20	10	5
ES-100ppb (µL)	0	16	18	19	19.6	19.8	19.9
MeOH (µL)	0	753	847	894	922	931	936
WATER (µL)	0	31	35	37	38.4	38.8	39
TOTAL (µL)	75	1000	1000	1000	1000	999.6	999.9
UNFORTIFIED ID-AQ/ID-SOLID DILUTION PREP							
EXTRACT (µL)	ALIQUOT	200	100	50	20	10	5
ES-100ppb (µL)	0	0	0	0	0	0	0
MeOH (µL)	0	768	864	912	941	950	955
WATER (µL)	0	32	36	38	39	40	40
TOTAL (µL)	75	1000	1000	1000	1000	1000	1000
In-vial 50X ID Screen							
In-vial 50X ID Screen		240µL 96%MeOH	+	5µL SUR 100ppb	+	5µL sample extract	
DAI DILUTION PREP							
SAMPLE (µL)	500	100	50	25	10	5	
ES (µL)	25	25	25	25	25	25	
MeOH (µL)	475	475	475	475	475	475	
Water (µL)	0	400	450	475	490	495	
TOTAL (µL)	1000	1000	1000	1000	1000	1000	
533 DILUTION PREP							
EXTRACT (µL)	950	200	100	50	20	10	5
IS (µL)	50	40	45	47.5	49	49.5	49.75
ES (µL)	0	40	45	47.5	49	49.5	49.75
80% MeOH (µL)	0	720	810	855	882	891	895.5
TOTAL (µL)	1000	1000	1000	1000	1000	1000	1000

NOTE: Serial dilution will be performed for dilutions higher than 200X.

APPENDIX G. MS/MSD, MS/FD SAMPLE SELECTION PROTOCOL

Background: EPA 537.1 and DOD QSM 5.3, Table B-15 both require that a matrix spike (MS) sample and a matrix spike duplicate (MSD) or field duplicate (FD) be prepped with every prep batch. Further, this SOP states that "every effort is made to ensure that an MS/MSD or an FD is included in every batch." Therefore, all aqueous prep batches must include an MS/MSD or MS/FD pair, if possible. Prep analysts will select samples to be used for this purpose following a hierarchy of preference. See below:

*****Any kind of blank (FB,TB,EB,RB,etc.) or samples designated as "DUP" by the client will not be used for MS/MSD/FD analysis.*****

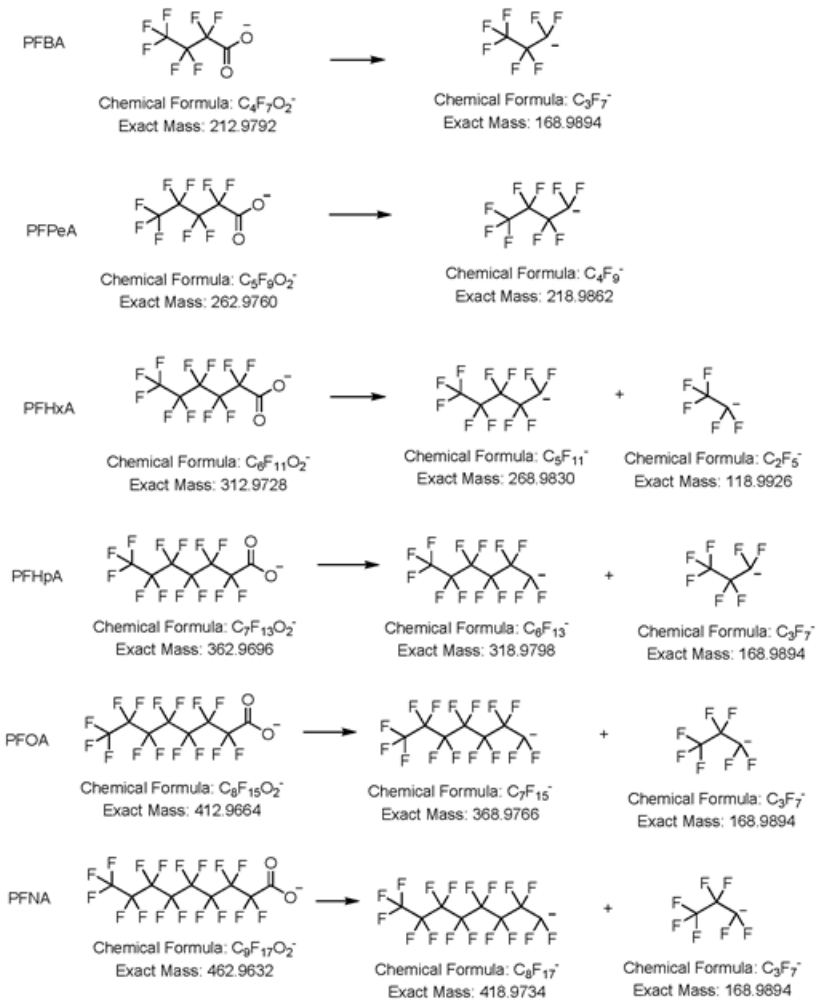
1. First preference is to use client-designated samples as MS/MSD samples. This designation should show up on the prep widget, under comments. It is possible that SR will miss adding this comment to the sample, but this designation will be present in the COC from the client, on the right side of the COC under "Remarks/Cooler ID." When a client designates a sample to be used for MS/MSD analysis, they will typically provide us with more than 2 bottles (often 4, sometimes as many as 6).

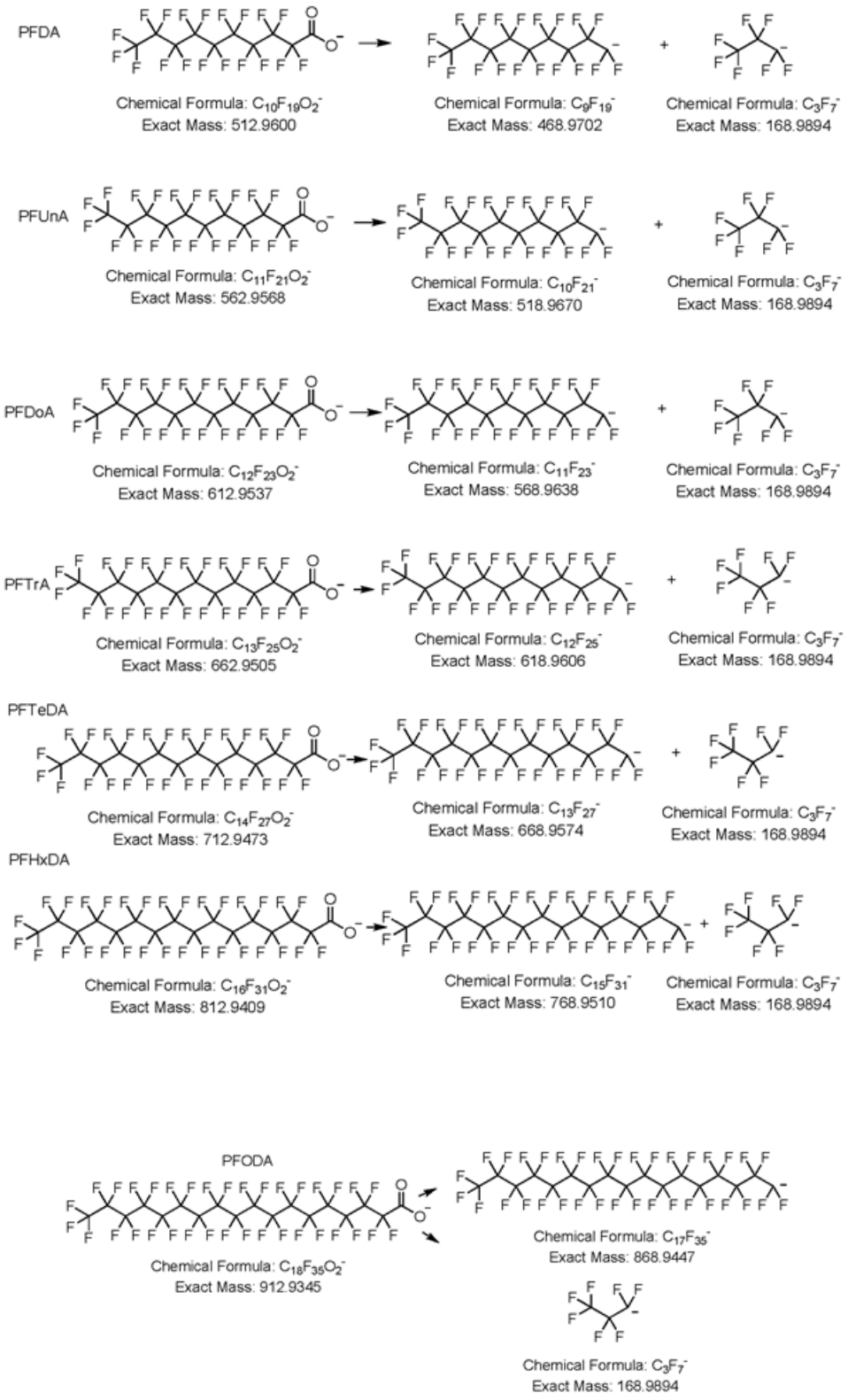
2. Lacking a client-designated MS/MSD sample, the next preference is to use any sample received with more than 2 bottles provided. If an analyst selects a set of samples for prep in which none of the samples are client-designated for MS/MSD, the analyst should check for any samples in the set that were received with 3 or more bottles. If there is a sample with 3 or more bottles, pull 3 of them and use one for the parent sample and spike the other two for analysis as MS/MSD samples.

3. Lacking any samples received with 3 or more bottles, the prep analyst must use two different samples to fulfill the MS/FD pair requirement. Find two samples out of the set of samples selected for prep which were received with 2 bottles, and pull both bottles for each sample. Pick one sample (pair of bottles) to be used for parent/MS prep and the other sample (pair of bottles) to be used for parent/FD. The sample selected for parent/MS will have one bottle spiked with targets and one prepped as normal, with no added spiking. The bottle which is spiked should be identified in the LIMS3 PB as MS (select parent sample in PB, click the MS/MSD button, then select the MSD sample and click the minus sign button to remove the MSD, leaving just the parent and MS). The sample selected for parent/FD will have both bottles prepped following normal procedures, but will have one of the two designated as DUP in the PB in LIMS3 (select parent sample in PB then click the "DUP" button to generate a DUP instance of the sample).

4. If all samples in a particular prep batch were all received in just one bottle, analysis of an MS/MSD or MS/FD pair will not be possible. In this case, the prep analyst will prep an LCS/LCSD pair and NCM all the samples in the PB for "MS/MSD – Insufficient volume – Ran LCS/LCSD". This should be a rare occurrence, as prep analysts will attempt to adjust batching to ensure that every PB contains an MS/MSD or MS/FD.

APPENDIX H. CHEMICAL DERIVATION OF ION TRANSITIONS




PFDA
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Chemical Formula: $C_9F_{19}^-$
Exact Mass: 468.9702
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFUnA
Chemical Formula: $C_{11}F_{21}O_2^-$
Exact Mass: 562.9568
Chemical Formula: $C_{10}F_{21}^-$
Exact Mass: 518.9670
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFDoA
Chemical Formula: $C_{12}F_{23}O_2^-$
Exact Mass: 612.9537
Chemical Formula: $C_{11}F_{23}^-$
Exact Mass: 568.9638
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFTrA
Chemical Formula: $C_{13}F_{25}O_2^-$
Exact Mass: 662.9505
Chemical Formula: $C_{12}F_{25}^-$
Exact Mass: 618.9606
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFTeDA
Chemical Formula: $C_{14}F_{27}O_2^-$
Exact Mass: 712.9473
Chemical Formula: $C_{13}F_{27}^-$
Exact Mass: 668.9574
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFHxDA
Chemical Formula: $C_{16}F_{31}O_2^-$
Exact Mass: 812.9409
Chemical Formula: $C_{15}F_{31}^-$
Exact Mass: 768.9510
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFODA
Chemical Formula: $C_{18}F_{35}O_2^-$
Exact Mass: 912.9345
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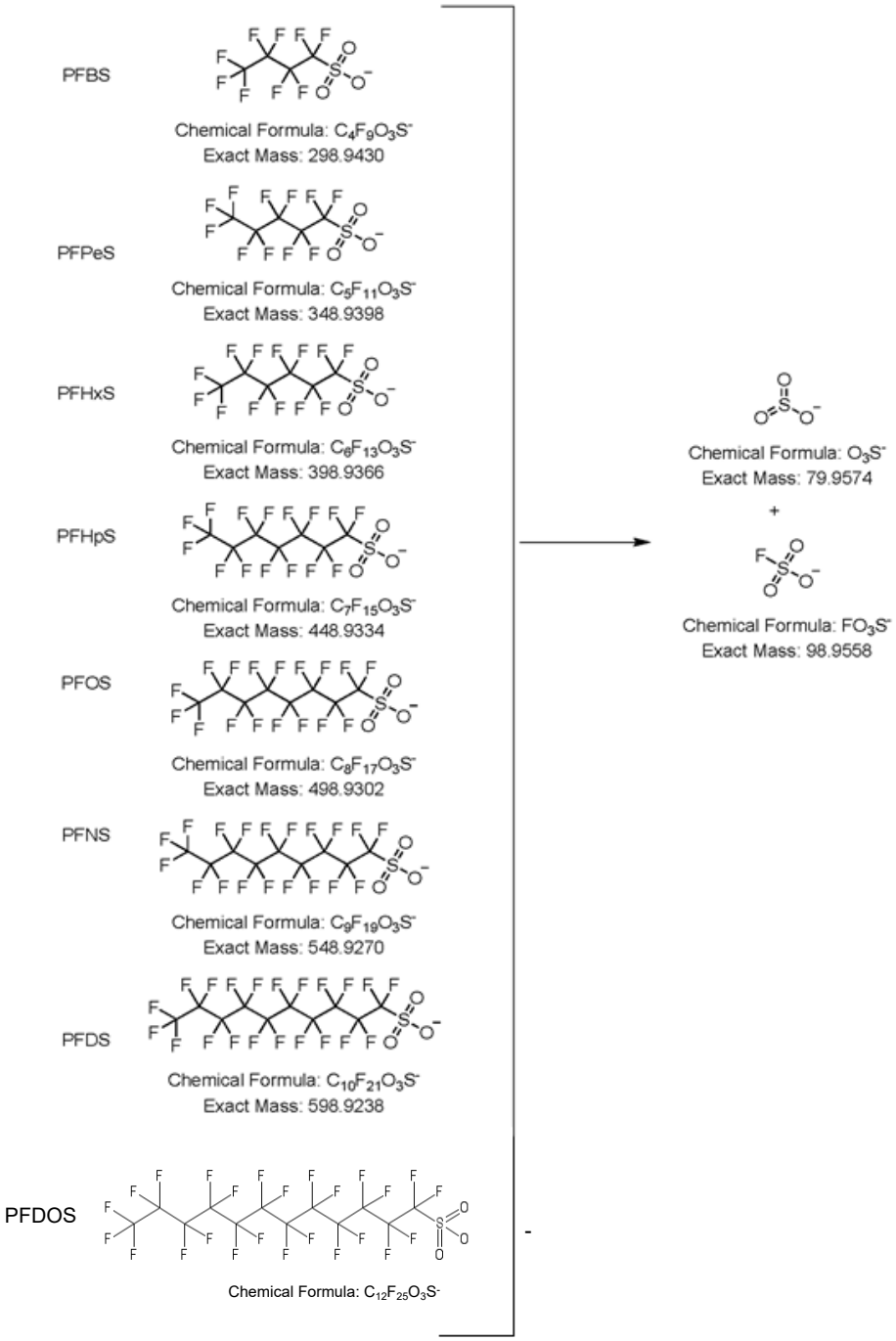
Exact Mass: 868.9447
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894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Chemical Formula: $C_4F_9O_3S^-$
Exact Mass: 298.9430
PFPeS
Chemical Formula: $C_5F_{11}O_3S^-$
Exact Mass: 348.9398
PFHxS
Chemical Formula: $C_6F_{13}O_3S^-$
Exact Mass: 398.9366
PFHpS
Chemical Formula: $C_7F_{15}O_3S^-$
Exact Mass: 448.9334
PFOS
Chemical Formula: $C_8F_{17}O_3S^-$
Exact Mass: 498.9302
PFNS
Chemical Formula: $C_9F_{19}O_3S^-$
Exact Mass: 548.9270
PFDS
Chemical Formula: $C_{10}F_{21}O_3S^-$
Exact Mass: 598.9238
PFDOS
Chemical Formula: $C_{12}F_{25}O_3S^-$
-
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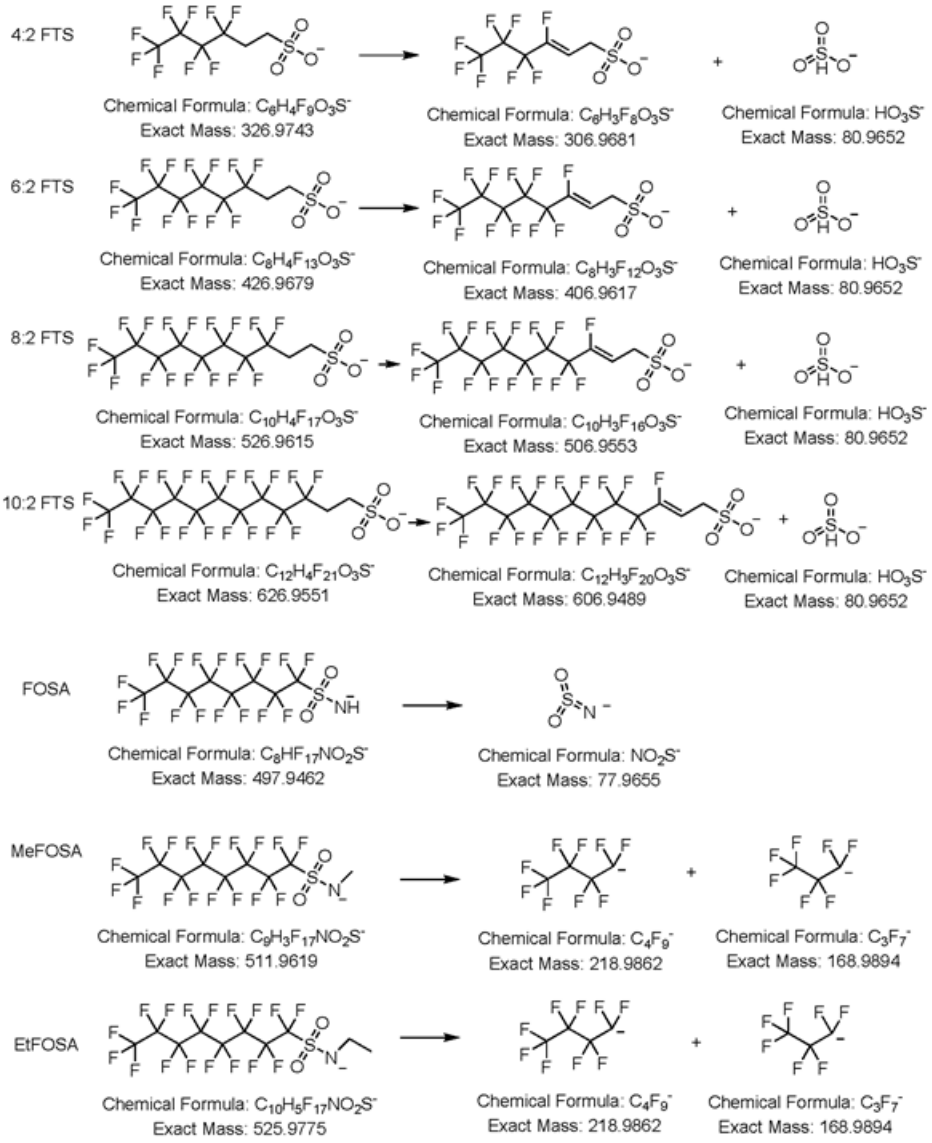
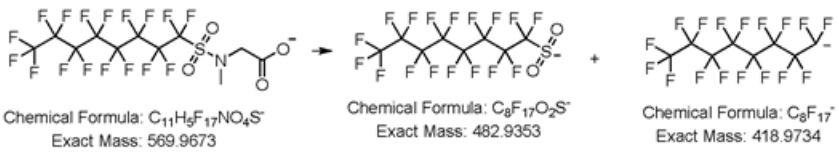
+
Chemical Formula: FO_3S^-
Exact Mass: 98.9558


4:2 FTS
Chemical Formula: $C_6H_4F_9O_3S^-$
Exact Mass: 326.9743
Chemical Formula: $C_6H_3F_8O_3S^-$
Exact Mass: 306.9681
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
6:2 FTS
Chemical Formula: $C_8H_4F_{13}O_3S^-$
Exact Mass: 426.9679
Chemical Formula: $C_8H_3F_{12}O_3S^-$
Exact Mass: 406.9617
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
8:2 FTS
Chemical Formula: $C_{10}H_4F_{17}O_3S^-$
Exact Mass: 526.9615
Chemical Formula: $C_{10}H_3F_{16}O_3S^-$
Exact Mass: 506.9553
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
10:2 FTS
Chemical Formula: $C_{12}H_4F_{21}O_3S^-$
Exact Mass: 626.9551
Chemical Formula: $C_{12}H_3F_{20}O_3S^-$
Exact Mass: 606.9489
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
FOSA
Chemical Formula: $C_8HF_{17}NO_2S^-$
Exact Mass: 497.9462
Chemical Formula: NO_2S^-
Exact Mass: 77.9655
MeFOSA
Chemical Formula: $C_9H_3F_{17}NO_2S^-$
Exact Mass: 511.9619
Chemical Formula: $C_4F_9^-$
Exact Mass: 218.9862
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
EtFOSA
Chemical Formula: $C_{10}H_5F_{17}NO_2S^-$
Exact Mass: 525.9775
Chemical Formula: $C_4F_9^-$
Exact Mass: 218.9862
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894

MeFOSAA

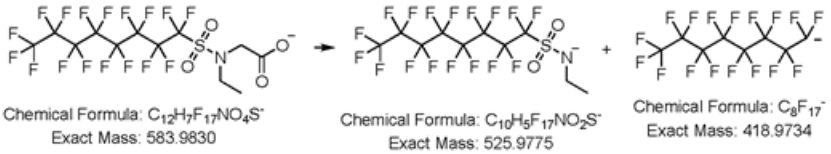


Chemical Formula: $C_{11}H_5F_{17}NO_4S^-$
Exact Mass: 569.9673

Chemical Formula: $C_8F_{17}O_2S^-$
Exact Mass: 482.9353

Chemical Formula: $C_8F_{17}^-$
Exact Mass: 418.9734

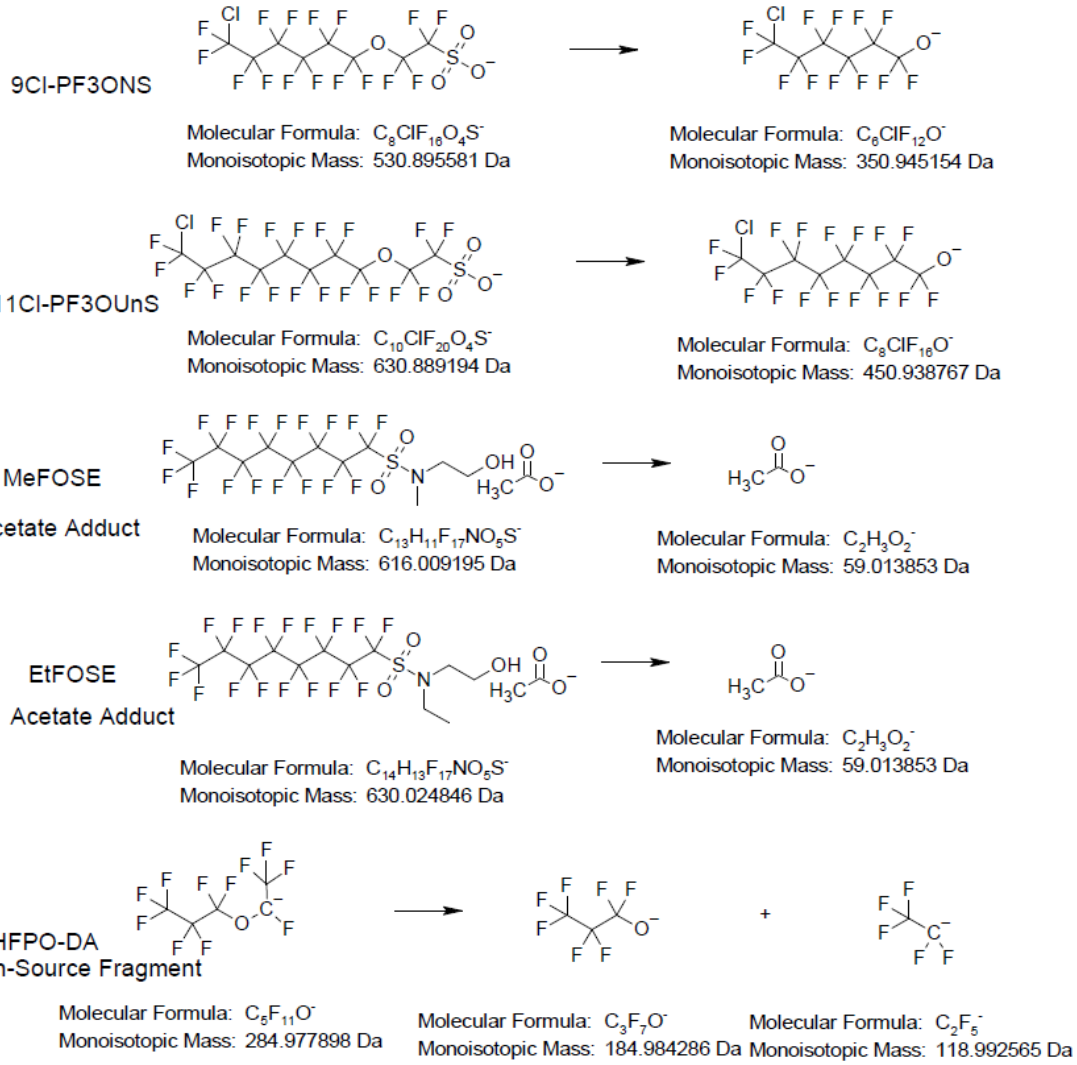
EtFOSAA



Chemical Formula: $C_{12}H_7F_{17}NO_4S^-$
Exact Mass: 583.9830

Chemical Formula: $C_{10}H_5F_{17}NO_2S^-$
Exact Mass: 525.9775

Chemical Formula: $C_8F_{17}^-$
Exact Mass: 418.9734


9Cl-PF3ONS
Molecular Formula: C8ClF16O4S-
Monoisotopic Mass: 530.895581 Da
Molecular Formula: C6ClF12O-
Monoisotopic Mass: 350.945154 Da
11Cl-PF3OUnS
Molecular Formula: C10ClF20O4S-
Monoisotopic Mass: 630.889194 Da
Molecular Formula: C8ClF16O-
Monoisotopic Mass: 450.938767 Da
MeFOSE
Acetate Adduct
Molecular Formula: C13H11F17NO5S-
Monoisotopic Mass: 616.009195 Da
Molecular Formula: C2H3O2-
Monoisotopic Mass: 59.013853 Da
EtFOSE
Acetate Adduct
Molecular Formula: C14H13F17NO5S-
Monoisotopic Mass: 630.024846 Da
Molecular Formula: C2H3O2-
Monoisotopic Mass: 59.013853 Da
GenX HFPO-DA
-CO2 In-Source Fragment
Molecular Formula: C5F11O-
Monoisotopic Mass: 284.977898 Da
Molecular Formula: C3F7O-
Monoisotopic Mass: 184.984286 Da
Molecular Formula: C2F5-
Monoisotopic Mass: 118.992565 Da

APPENDIX I: DOD/DOE QSM REQUIREMENTS

Sections found in this appendix replace and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense, as stipulated in the DOD Quality System Manual.

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., Aqueous Film Forming Foam (AFFF) formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. 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.

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
AFFF and AFFF Mixture Samples 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.
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF and AFFF Mixture 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 instructions on corrective maintenance.	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an 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).

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
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 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.	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 quantitative analysis.

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 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) using 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. *(continued next page)*	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.

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) *(Continued)*		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 $r^2 \geq 0.99$ for each analyte.			
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.
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. Analytes 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.

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
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.
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.

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
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 (>1/2 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 samples 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 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 (EIS) 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% to 150% of 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 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-extract 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 (MS)	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 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. 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 is ≥ 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 as < 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.