Per- and Polyfluoroalkyl Substances (PFAS) Nevada Division of Environmental Protection (NDEP) Sampling Project

FINAL Quality Assurance Project Plan (QAPP)

September 27, 2023

Prepared by:

Broadbent & Associates, Inc.

and

GHD Inc.

on behalf of the

Nevada Division of Environmental Protection

Approvals:

Broadbent Project Coordinator: Josh Fortmann

Signature: Joshua Fortmann Digitally signed by Joshua Fortmann Date: 2023.10.03 15:31:43 -07'00' Date: _____

Nevada Division of Environmental Protection (NDEP) Team Leader: Michael Antoine

Signature: Michael R. Antoine Digitally signed by Michael R. Antoine Date: 2023.10.03 09:09:51 -07'00' Date: _____

NDEP QA Manager: Michael Antoine

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U.S. Environmental Protection Agency (EPA) Region 9 QA Manager: Audrey Johnson

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A2 – Table of Contents

Appendices

A3 – Distribution List

The following is a list of key project personnel and their responsibilities:

Contact Name / Organization	Responsibility	Location	Phone	Email
Michael Antoine / NDEP	NDEP Team Leader	Carson City, NV	775-687-9490	mantoine@ndep.nv.gov
Michael Antoine / NDEP	QA Manager	Carson City, NV	775-687-9490	mantoine@ndep.nv.gov
Audrey Johnson / EPA	Region 9 Quality Assurance Manager	San Francisco, CA	415-947-8000	johnson.audreyl@epa.gov
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Josh Fortmann / Broadbent	Project Coordinator	Reno, NV	775-322-7969	jfortmann@broadbentinc.com
Kevin Calcagno / Eurofins	Laboratory Point of Contact	Sacramento, CA	916-960-7479	kevin.calcagno@et.eurofinsus.com
Eduardo Rodriguez / Eurofins	Laboratory Director	Pomona, CA	626-386-1138	eduardo.rodriguez@et.eurofinsus.com
Caroline Sangari / Eurofins	Business Unit Manager	Pomona, CA	626-827-9817	caroline.sangai@et.eurofinsus.com
Multiple*	Sampling Leader	N/A	N/A	N/A

* Sampling leaders will be selected by Broadbent and will vary based on the specific Facility or Site.

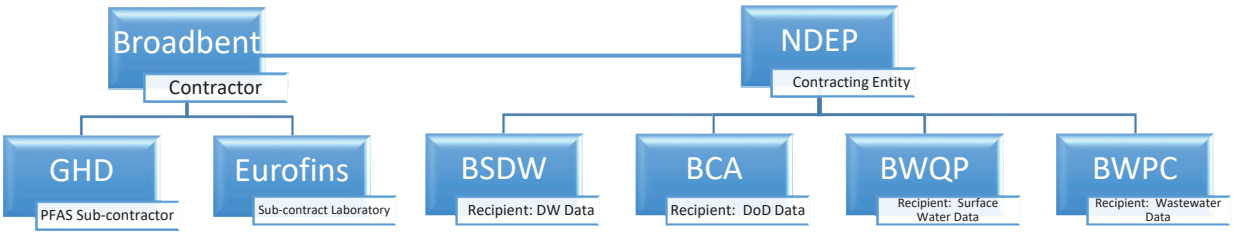
A4 – Project Organization

A4.1 – Organizational Roles and Responsibilities

The Nevada Division of Environmental Protection (NDEP) is the contracting entity, having solicited bids for PFAS sampling and analysis through the Request for Proposal (RFP) process. Michael Antoine is the NDEP contract monitor for this effort and will be responsible for the overall technical management of this contract. Mr. Antoine is also the NDEP Quality Manager for this contract and will be responsible for ensuring the usability of data for the four data recipient Bureaus within NDEP.

Broadbent and Associates is the environmental consulting firm that won the competitive bid and was awarded the PFAS sampling and analysis contract. Joshua Fortmann is a Certified Environmental Manager and is the Broadbent Project Coordinator for this effort, responsible for the day-to-day management of the contract. GHD is a global, professional services company that has been subcontracted by Broadbent to provide PFAS expertise for this contract. Eurofins Eaton, LLC (Eurofins), is the Nevada certified environmental testing laboratory that that has been subcontracted by Broadbent to provide PFAS analytical services.

A4.2 – Organization Chart



A5 – Problem Definition and Background

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals that have been in use since the 1940s. PFAS are found in a wide array of consumer and industrial products. PFAS manufacturing and processing facilities, facilities using PFAS in production of other products, airports, and military installations are some of the contributors of PFAS releases into the air, soil, and water. Due to their widespread use and persistence in the environment, most people in the United States (US) have been exposed to PFAS. Studies show that certain PFAS compounds are persistent in the environment, bioaccumulate, and are toxic to lab animals and associated with adverse health effects in humans (including testicular cancer, kidney cancer, high cholesterol, pre-eclampsia, and thyroid problems).

There are thousands of PFAS, but the most extensively produced and studied of these chemicals are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). In 2022, the EPA issued an interim updated health advisory for PFOA of 0.004 parts per trillion (ppt) and for PFOS of 0.02 ppt, replacing those issued in 2022. EPA published a PFAS Strategic Roadmap in 2020, laying out likely further action from federal regulatory agencies. The health advisory offers a margin of protection from adverse health effects for all individuals, including babies exposed during pregnancy, nursing infants, children, and those exposed over a person's lifetime. More PFAS information is available at the United States Environmental Protection Agency's (EPA) website: www.epa.gov/PFAS.

Interpreting data from analysis of PFAS in a variety of environmental sample types can be challenging due to variations in analytical protocols, quality control types and criteria, and data review procedures across laboratories and general ubiquity in the environment. Moreover, PFAS are analyzed at the parts per trillion level, leaving little tolerance for cross-contamination of samples. Stringent quality control and adherence to sampling protocol is needed to ensure data quality and reliability to allow information

decisions regarding site specific actions. This document outlines the level of quality control necessary such that any sample analyzed and reviewed can be relied upon for decision making purposes.

A6 – Project Description

This Quality Assurance Project Plan (QAPP) presents the policies, organization, objectives, functional activities, and quality assurance/quality control (QA/QC) activities designed to achieve the specific data quality goals to conduct sampling of drinking water sources, treated wastewater outfalls, and surface water at various facilities and sites. PFAS are not regulated under the Safe Drinking Water Act (SDWA), and therefore, there are no sampling requirements nor are Maximum Contaminant Levels set for these compounds. This voluntary sampling effort by NDEP will work to fill in the information gap where there is no testing currently being conducted and no regulatory authority for it to be required. As the data will not be compliance data, NDEP's actions will be limited to informing the applicable contacts and making recommendations that will vary on a case-by-case basis. The goal of the project is to inform the NDEP about the potential sources of PFAS in drinking water and to provide a basis for NDEP to address the potential issue of PFAS in drinking water beyond this sampling project.

Samples will be collected from Public Water Systems, Wastewater Treatment Plants, Publicly Owned Treatment Plants, State Water Bodies, Outfalls and identified Stream Reaches, to determine PFAS concentrations. Sampling will be coordinated and conducted by Broadbent & Associates, Inc. (Broadbent) with assistance from available facility operators. A Sampling Standard Operating Procedure (SOP) is provided in Appendix A to ensure a consistent methodology is followed to minimize variables in results. The SOP includes methodologies for drinking water, surface water, and treated wastewater sample collection.

The laboratory selected for this project (Eurofins) will report compounds identified in the methods as determined by sample source shown in Appendix B. Eurofins is a Nevada certified laboratory for PFAS analysis. All analyses will be conducted using approved EPA-methods 533 and/or 537.1 for drinking water samples and DRAFT EPA Method 1633 for other aqueous (e.g., treated wastewater, surface water) samples.

A6.1 – Objective and Scope Statement

NDEP is implementing a voluntary monitoring program to characterize PFAS concentrations in tested areas of Nevada. Sampling priorities are based on potential PFAS sources and their proximity to drinking water protection areas. Broadbent will raise awareness of potential water quality issues with respect to PFAS by communicating analytical results to NDEP and the regulated community and by providing educational materials on how to address PFAS contamination if necessary. This project will create local partnerships between Public Water Systems, local businesses, waste dischargers, and the communities they serve.

The project objectives are to provide sampling and analysis which will provide data with an acceptable level of accuracy and precision to determine the extent (if any) of PFAS in Nevada drinking water sources. Broadbent, with assistance from available facility operators, will collect the samples and may provide guidance on mitigation procedures. Sampling will begin in 2023 and continue until all facilities/sites to be sampled are tested, or as many as the budget and time constraints allow. This effort

will cover the initial sampling of a group of NDEP facilities and sites with the potential for follow up sampling at the discretion of NDEP for sampling locations that register concentrations above the EPA's 2022 interim Health Advisory Limit (HAL).

A6.2 – Data Usage

Broadbent will summarize sample laboratory analytical results the analytical for presentation to NDEP. As there is no regulatory requirement, data usage for this project will be limited to informing NDEP and making recommendations on a case-by-case basis. Environmental PFAS data will be compiled in a format suitable for ingestion into various NDEP databases to enhance PFAS decision making capabilities and to facilitate possible future development of a PFAS fate and transport risk assessment modeling tool. This data may be used to inform future NDEP decision making after a drinking water regulation is established for any PFAS sampled in this project.

A6.3 – Schedule of Tasks and Products

Project will be initiated in Summer 2023:

Early June 2023 – Draft QAPP Submittal

Mid-June 2023 – Begin sampling coordination with facilities

Early July 2023 – Receive Draft QAPP comments and submit Final QAPP

Mid-July 2023 – Commence sampling activities

Mid July through TBD – Sampling window for remaining facilities/sites. Will be conducted on a rolling basis.

The timeline will largely be defined by approval of the QAPP and coordination of facility access and will operate on a rolling basis for each facility/site individually. Broadbent will schedule sampling events following the priority list provided by NDEP.

Table 1 represents a typical schedule for each site.

Activity	Timeframe
Confirm Site Sampling Locations	~1 week
Receive Sample Bottles and Sample Training	1-2 weeks
Sampling (per site/facility)	1 day
Send Samples to the Lab	<2 days
Lab Processing	~1 month
Notifying NDEP	1-2 weeks
Potential Follow Up	TBD

Table 1 Project Timeframes (As of 9/26/2023)

Broadbent will continue to sample all NDEP identified facilities/sites; therefore, no specific timeline is given. The project schedule depends upon several variables – facility/site response times, availability of samplers, schedule of the laboratory – this may change as the project develops.

A7 – Quality Objectives and Criteria

A7.1 – PFAS Quality Objectives

The quality objective is to give NDEP information about drinking water quality at various facilities/sites regarding PFAS concentrations in water.

Management decisions regarding the control of PFAS in drinking water are based on the ability to reliably detect and quantify PFAS in drinking water. For PFAS, the possibility of outside contamination of samples is high, and the target action level concentrations are in the low parts per trillion range. To reliably achieve such low analytical detection and reporting limits, and to assure samples are free of outside contamination, robust sampling and analysis protocols and analytical methods are required. The generation of quality data is a process which relies on planning at the outset of a sampling project. The data verification process may identify potential sampling errors, such as preservation and sample handling methods, which are out of conformance with the sampling plans' data quality objectives.

Data will be acceptable if 1) approved SOPs are followed to ensure outside contamination is not introduced, 2) appropriate QA/QC samples are collected to ensure outside contamination is not present from either the laboratory or sampling methodology, 3) data generated can be verified or validated through established procedures listed in Section D of this QAPP, and 4) the detection limits achieved from the analysis are below the lab-specified minimum reporting levels (MRL).

A7.2 – QC Performance criteria for water chemistry

A7.2.1 – Field Precision

Precision of the field sample collection procedures will be assessed by the analysis of field duplicate samples. Field duplicate samples will be collected at a frequency of 1 per 10 or fewer samples or at a minimum frequency of 1 per sampling event. The samples will be labelled such that the field duplicate sample is "blind" to the laboratory. A relative percent difference (RPD) of 50 percent for water samples will be used as the acceptance limit for analytes detected in both the investigative and field duplicate samples at concentrations greater than or equal to five times their quantitation limits.

A7.2.2 – Laboratory Precision

Laboratory precision will be assessed through the calculation of RPDs for laboratory duplicate sample analyses. These will be matrix spike/matrix spike duplicate (MS/MSD) and/or laboratory control samples/laboratory control sample duplicates (LCS/LCSD). The equation to be used to determine precision is presented in Section E1.1of this QAPP. Laboratory precision acceptance criteria will be generated by the laboratory and included in the laboratory reports.

A7.2.3 – Field Accuracy

The criteria for accuracy of the field sample collection procedures will be to ensure that samples are not affected by sources external to the sample, such as inadequate equipment decontamination procedures or sample contamination by ambient conditions or sample cross contamination. Field sampling accuracy will be assessed using the data from equipment blank samples, and field blank samples.

Equipment blank samples will be collected at a minimum frequency of 1 per 20 or fewer samples or 1 equipment blank per day, whichever is most frequent, when non-dedicated sampling equipment is used. Equipment blank samples will be collected by routing laboratory grade deionized (DI) water over decontaminated sampling equipment (e.g., sampling pole) for the same parameters being analyzed for the investigation collection activities. Equipment blank samples are collected, preserved, and shipped in an identical manner as field samples. The purpose of equipment blanks is the assess the adequacy of the decontamination process, assess contamination from the total sampling event, sample preparation and measurement process where decontaminated sample equipment is used to collect samples as opposed to one-time use equipment. An equipment blank captures the ambient environmental conditions that a field blank is intended to capture but will not distinguish detections related to equipment conditions versus ambient conditions.

A field blank sample will be collected at a minimum frequency of one per event. Field blanks are prepared by laboratory grade DI water into sample bottles for the same parameters being analyzed for the investigation collection activities and are preserved and shipped in an identical manner as field samples. The purpose of the field blank sample is to assess ambient contamination from field conditions during sampling.

The samples will be labeled such that the equipment and field blank samples are "blind" to the laboratory.

Equipment, and field blank samples should not contain target analytes. The blank sample data will be evaluated using the procedures specified in E1.2 of this QAPP. Accuracy also will be ensured by adhering to all sample handling procedures, sample preservation requirements, and holding time periods.

Accuracy of field measurements will be assessed by analyzing calibration check samples, as applicable to the parameter being measured.

Additional types of field QC samples used in this project are described in Section B5.

A7.2.4 – Laboratory Accuracy

Laboratory accuracy will be assessed by determining percent recoveries from Laboratory Control Sample (LCS) analyses. An LCS will be analyzed at a frequency of 1 per laboratory batch of 20 or fewer samples of the same matrix. Accuracy relative to the sample matrix will be assessed by determining percent recoveries from the analysis of matrix spike (MS) samples. The equation to be used to determine accuracy for this project is presented in E1.2 of this QAPP. Laboratory accuracy acceptance criteria will be generated by the laboratory and included in the laboratory reports.

Quality control (QC) samples will be collected at rates consistent with the analytical method(s). The results will be evaluated as described in the applicable section of the PFAS method used and US EPA Data Review and Validation Guidelines for PFASs (US EPA, 2018a).

A7.3 – Data Representativeness

The sampling effort is designed to identify potential sources of PFAS near drinking water system. Sampling at facilities/sites will be conducted at locations closest to the source intake.

Under this QAPP, PFAS sampling and analysis method activities will be primarily focused on characterizing PFAS concentrations in drinking water sources in selected areas of Nevada. Priorities will be set based on potential contaminant sources and their proximity to drinking water protection areas.

A8 – Special Training

Sample collection personnel will be trained by Broadbent to ensure they follow the Sampling SOP (Appendix A) to minimize PFAS introduction during sampling. Broadbent will maintain training records of sampling personnel. When field reagent blanks have PFAS present, replicate sample results are inconsistent, or when procedures are not being followed, additional training will be provided. Laboratory personnel training records are maintained by the laboratory. The groundwater laboratory is required to be accredited by the National Environmental Laboratory Accreditation Program (NELAP) to demonstrate compliance with EPA's requirement that the laboratory have a documented quality system that complies with American National Standards Institute/American Society for Quality Control (ANSI/ASQC) E4 94 ("Specifications and Guidelines for Quality System for Environmental Data Collection and Environmental Technology Programs", January 1995), and EPA QA/R 2 ("EPA Requirements for Quality Management Plans", March 2001). The groundwater laboratory is accredited by NELAP for the analyses identified in this QAPP.

A9 – Documents and Records

The final QAPP will be provided to the appropriate project personnel through email by the Project Coordinator as detailed in the distribution list. Draft and final QAPP versions will be sent to each person on the distribution list via email or file sharing if the file exceeds 20 megabytes. The date of revision will be included in the document name and in the footer of the document.

The chain-of-custody and any other sampling-related forms shall be maintained in their original form by the authorized sample collector. Information from contractors and sampling personnel will be maintained as required by NDEP. Sample collection personnel will submit all original forms to the Project Coordinator. The contractor will summarize the analytical results for samples submitted and provide method detection limits (MDLs), quantitation limits (MLs or PQLs), data qualifiers, and associated quality control results in a data report (electronic and paper copies), as well as providing a narrative summary of quality control measurement results and both the paper and electronic reports to the NDEP in a timely manner (within 2 months of sample delivery to laboratory). Data should be censored at the MDL, with results above the MDL and below the QL reported “as is” with an estimated (J) qualifier. Results less than the MDL should be reported as the value of the MDL, with a U qualifier (non-detect). Results greater than the quantitation limit (ML or PQL) is reported “as is” without a U or J qualifier.

All PFAS analytical results will be provided in an electronic format agreed upon by NDEP to facilitate ingestion into Bureau of Water Quality Planning (BWQP), Bureau of Water Pollution Control (BWPC), Bureau of Corrective Actions (BCA), and BSDW databases, and the PFAS Risk Assessment Modeling tool. Data shall be provided in tabular format. For samples collected at public water system source locations (wells, springs, intakes), the data should contain the unique identifier for the public water system feature (PWS ID Number and State Assigned Identification ID, e.g., NV0000190 W33). Coordinates in

decimal degrees (North American Datum of 1983 [NAD 83]) may also be provided for additional accuracy. For samples collected in other locations, coordinates must be provided.

The format for all data recording will be consistent with the requirements and procedures used for data assessment, verification and validation described in this QAPP. Files generated according to applicable standard operating procedures (such as raw data, results of QC checks, problems encountered, etc.) will be documented and reported to the Project QA Officer.

All communications regarding study plan changes or refinements, such as changes to facilities/sites, staff, parameters, etc. will be filed by the Project Coordinator.

All PFAS concentrations at or above the EPA's 2022 interim HAL will be communicated to NDEP within 96 hours of final level review and laboratory management's approval/validation of the analytical batch in which the exceedance was detected. Electronic data for inclusion into these various databases may be provided subsequent to the laboratory report and/or detection notification required.

A9.1 – Document/record control

The recording media for the project will be a combination of PFAS-free paper and electronic means to document site conditions. Data gathered using paper will be recorded using pen, and changes to such data records will be made by drawing a single line through the error with an initial by the responsible person. Similar methods will be used for electronic data recording.

Agency management, Project Coordinator, and Quality Assurance Managers will approve updates to the QAPP, as needed. The Project Coordinator shall retain copies of all management reports, memoranda, and all correspondence between team members. Retention of records should emphasize any deviations from the signed QAPP, including the rationale for those changes.

A9.2 – Document storage

The Project Coordinator will maintain a central project directory, that will act as a repository for all data collected or generated as part of this project.

Broadbent will maintain project records on Broadbent servers location for a duration of five years. Broadbent server data is backed up on cloud servers. All files will be retained by NDEP according to the NDEP records retention policy. The laboratory will maintain all records consistent with the laboratory's record retention policies.

B1 – Sampling Process Design

General sampling design is described below. Broadbent will work with each facility/site to identify and confirm sample collection locations and sampling logistics.

Eurofins Eaton Analytical (Pomona, CA) will be used for analysis of drinking water samples by US EPA Method 533 and 537.1, and Eurofins Test America (West Sacramento, CA) will be used for analysis of outfall and surface water samples for US EPA proposed Method 1633.

B1.1 – Types and numbers of samples required

The number of samples will vary depending on the site. Water samples will be collected from public water systems, wastewater treatment plants, publicly owned treatment plants, state water bodies, outfalls and identified stream reaches. At minimum, a water sample and field reagent blank (FRB) will be collected at each identified sampling location. Collected water will be preserved using appropriate methods, as outlined in Appendix A and U.S. EPA Method 533 (US EPA, 2019), U.S. EPA Method 537.1, or proposed U.S EPA Method 1633. All sample types will be indicated on the chain of custody.

B1.2 – Design of the sampling

Samples will be discrete grab samples from each facility/site.

B1.3 – Sampling locations and frequencies

The sampling sites will consist of priority drinking water source sites, outfalls, and surface water bodies as provided by the NDEP in Appendix C. For this project, the initial samples will be taken at designated facility/site locations. NDEP may request follow up sampling if PFAS are detected above Health Advisory Levels. in the initial sample.

If any site cannot be sampled due to access issues, the contractor shall communicate with NDEP in taking provisional action to identify an alternate site or assist in gaining access if feasible.

Pre-Sampling Procedures

Broadbent will work with the facility/site to coordinate a schedule for sampling. A proposed date/time of sampling must meet the following criteria:

- Sufficient time allowed for the sampler to access the facility/site.
- Coordination with facility/site management.
- Coordination with the laboratory so they can schedule analysis and indicate when results will be available.

Sampling

- Once the pre-sampling procedures have been completed, the Project Coordinator will identify which locations will be sampled, authorize samples to be taken and direct the sampler. The PM will authorize any follow up sampling events with approval of NDEP.

  The PM will document any decisions made to authorize samples that deviate from the process shown in Figure 2 – this may occur because of questions in sampling procedures or samples close to the threshold.

- Sample Bottle Delivery and Pick-up
  - The sample kit will be sent to the authorized sampler
  - Included in the package will be:
    - Sample bottles (number of bottles to be agreed upon prior to mailing)
    - Cooler

        - Sampling SOP
        - Sampling form (Appendix D)
        - Chain of Custody (Appendix E)
        - Return shipping label

- Sampling Teams
    - **Two-person sampling teams are recommended**. Distributing the workload to ensure attention to the Sampling SOP (Appendix A) is easier with a two-person team. Also, having another team member present will increase awareness to conditions and actions that can adversely affect the quality of the sampling effort. Team members should watch each other's movement and activities where possible and identify immediately if someone is observed not following protocol.
    - When sampling for PFAS, a two-person team allows one person to be a dedicated "sample" handler, and the other person the dedicated "document" handler. One team member obtains the samples, and the other team member records the samples on the COC form with the sample collection information. If only one person is conducting the sampling, ensure care is taken to properly record all samples on the COC, and follow all the precautions noted in this guidance.

- Shipping
    - The authorized sample collector must schedule collection and delivery dates so that samples are received by the laboratory **within 48 hours of having been collected**. For this reason, it is preferrable for samples to be collected on Mondays, Tuesdays, and Wednesdays.
    - After the sample is taken, it must be extracted at the laboratory within 28 days of sampling.
    - The sample shall be shipped on ice to the laboratory by overnight mail.
        - Cooler specific instructions will be provided by the laboratory as part of bottle order shipments
        - See Appendix A for lab address and contact information

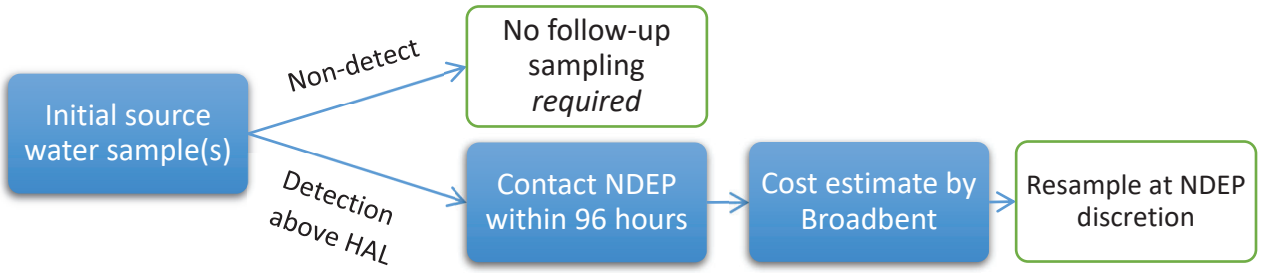


Figure 1 Sample Process Flow Chart

B2 – Sampling Method

All initial and follow-up samples will be collected as grab samples and according to the instructions within this document and as provided in Appendix A.

Table 3 in Section B4 presents a summary of the sample containers, sample volume, preservation requirements, and maximum holding time. Sample containers and bottles will be pre-preserved, pre-cleaned, and will not be rinsed prior to sample collection.

Sample collectors shall conduct all sampling activities in a manner to minimize potential contamination and cross-contamination of samples. The sample collector will thoroughly wash hands prior to wearing new nitrile gloves at each sampling point in order to avoid exposure to pollutants and other chemical, physical, and biological hazards, and to prevent cross-contamination of samples. The sample collector will not touch the insides of bottles or lids and caps during sampling.

All chemical data, field data, and data analysis methods and procedures in this document follow those specified in U.S. EPA Method 533 (US EPA, 2019).

B3 – Sample Handling and Custody

Sample handling shall be consistent with the Sampling SOP in Appendix A. Sample handlers should complete the chain of custody form before sampling, with any technical assistance needed from contractors.

A unique number will be assigned to each sample. Upon collection, each sample will be labeled and include sample ID, date/time, sampler initials, preservative, and analysis requested.

Sample Nomenclature

In order to maintain an organized sampling scheme, the PMs and field staff members will implement the following formatting rules when naming samples.

Facility/Site ID # - This is a unique identifier assigned to every facility/site by the NDEP.

Sample ID Format:

- [Sample Point ID]-[QA/QC Type (if applicable)]
- Example 1 – Field reagent blank: XXXXXXFRB
- Example 2 – Field sample collected: XXXXX

The components of these sample name formats are as follows:

1. Sample Point ID – This is an alphanumeric code that uniquely identifies each pre-defined sample point.
2. QA/QC Type (if applicable) - QC type codes should be included for QC samples and are listed below in Table 2.

	Description
Sample Point ID	Unique identifier assigned by the NDEP
XXXXXXX	Unique Sample ID describing the point where the sample was collected
QA/QC Type	This describes the type of QA/QC sample when applicable
-FRB	Field Reagent Blank
-DUP	Duplicate

Table 2 Sample Nomenclature

B4 – Analytical Methods

Analyte	Sample Matrix	Analytical Method Reference	Sample Container	Sample Preservation	Holding Time
PFAS analytes (Appendix B Table 1)	Drinking Water	USEPA 533	250 mL Polypropylene or HDPE	Ammonium acetate 1.0 g/L 6° Celsius	28 days
PFAS analytes (Appendix B Table 2)	Drinking Water	USEPA 537.1	250 mL Polypropylene or HDPE	Trizma 5.0 g/L 6° Celsius	14 days
PFAS analytes (Appendix B Table 3)	Surface Water Treated Wastewater	Proposed USEPA 1633	1-500 mL Polypropylene or HDPE 1-250 mL Polypropylene or HDPE	6° Celsius	28 days

Table 3 Sample Equipment and Methodology

Samples will be submitted with a 10 day turnaround time from the laboratory. The laboratory will be responsible for sample disposal following analysis. Detailed procedures for analytical methods are provided in Appendix F.

B5 – Quality Control

Due to the required low detection limits of PFAS in drinking water, EPA Method 533 and EPA Method 537.1 require the use of a field reagent blank (FRB) sample at the same time that the field sample (source sample) is collected. These special QC samples must be discussed with the laboratory prior to sampling to ensure proper sample containers and materials are on hand when sampling begins in the field. Duplicate QC samples will be collected at a 10% rate of primary samples and MS/MSD QC samples will be collected at a 5% rate of primary samples.

Quality control samples will match those described in U.S. EPA Method 533 (US EPA, 2019), US EPA Method 537.1, or proposed US EPA Method 1633.

FIELD REAGENT BLANK (Required for EPA Method 533 and EPA Method 537.1)

A FRB is analyzed to assess the potential for PFAS cross-contamination being introduced during the sampling process. The FRB consists of a pre-preserved sample bottle filled by the laboratory with PFAS-free water and shipped to the site with the other sample bottles. For each FRB, an empty sample bottle (with no preservative) must also be included. At the sample site, the sampler will open the FRB and pour it into the empty sample bottle. An FRB must be collected at each sample site (i.e., each source being sampled) and placed in the ice chest used to store and transport samples.

FIELD SAMPLE (Required)

The Field Sample is the sample collected from the source at a location prior to any treatment, to qualify as a "source sample". Drinking water samples will be collected at the closest feasible access point to the source intake.

B6 – Instrument/Equipment Testing, Inspection, and Maintenance

All laboratory equipment will be tested, inspected, and maintained in accordance with the applicable method(s) approved by the laboratory and the National Environmental Laboratory Accreditation Council (NELAC) Standard. There are no field instruments anticipated for this project.

B7 – Instrument/Equipment Calibration and Frequency

Instrument calibration of instrumentation is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established reporting limits. Each instrument is calibrated with standard solutions appropriate to the type of instrument and the linear range established for the analytical method. The frequency of calibration and the concentration of calibration standards are determined by the manufacturer guidelines, the analytical method, the National Environmental Laboratory Accreditation Council (NELAC) Standard, or the requirements of special contracts.

A bound notebook will be kept with each instrument requiring calibration in which will be recorded activities associated with the QA monitoring and repairs program. These records will be checked during periodic equipment review and internal and external QA/QC audits.

B8 – Inspection/Acceptance of Supplies and Consumables

Supplies and consumables will be inspected and accepted for use by the laboratory, in accordance with the laboratory's SOP and the NELAC Standard. As a Nevada certified laboratory, the laboratory is required to have a policy and procedure(s) for the selection and purchasing of services and supplies it uses that affect the quality of the environmental tests. Procedures shall exist for the purchase, reception and storage of reagents and laboratory consumable materials relevant for the environmental tests.

The laboratory shall ensure that purchased supplies and reagents and consumable materials that affect the quality of environmental tests are not used until they have been inspected or otherwise verified as complying with standard specifications or requirements defined in the methods for the environmental tests concerned. These services and supplies used shall comply with specified requirements. Records of actions taken to check compliance shall be maintained.

B9 – Non-direct Measurements

There are no Non-direct measurements required for this project.

B10 – Data Management

Each PFAS data result obtained from a facility/site will be identified by the Sample Point ID. Data shall be provided in tabular format. For samples collected at public water system source locations (wells, springs, intakes), the data should contain the unique identifier for the public water system feature (PWS ID Number and State Assigned Identification ID, e.g., NV0000190 W33). Coordinates in decimal degrees (WGS 84 or NAD 83) or UTM's may also be provided for additional accuracy. For samples collected in other locations, coordinates must be provided. The data generated from the project are not compliance data.

B10.1 – Laboratory Data Management

The data will be maintained in an electronic or hard-copy format. All material records will be maintained for the full duration of the project.

B10.2 – Data Management Summary

The Project Coordinator will maintain the project file in a dedicated folder. The objective is to have a complete record of all decisions about modifications of data collection, assessment, verification, validation, or interpretation between the QAPP signoff and project report completion. Data received from the laboratory will be stored by Broadbent on their servers for a duration of five years. The laboratory will maintain all records consistent with the laboratory's record retention policies.

The data will be collected with the following documents that will be completed for this project:

1. Chain of Custody Form (Appendix E): All pertinent sampling information will be recorded on a sampling form, including (but not limited to): Sample Point ID, sample time, and any other pertinent observations. A digital copy of the Chain of Custody should be emailed to the Project Coordinator. The hard copy of the Chain of Custody form will be mailed along with the samples to the laboratory.
2. Laboratory reports
    a. Laboratory reports will be sent to the PM
    b. The PM will notify the sampler

The documents may be converted into electronic versions. The PM will be responsible for maintaining the data from the COC and Lab reports.

Broadbent will consult with NDEP to analyze the data and make recommendations. The implementation of any recommendations is beyond the scope of this project.

C1 – Assessments and Response Actions

C1.1 – Assessments

Periodic assessment of facility/site sample sites, field equipment, and laboratory equipment is necessary to ensure that sampling is efficient, and data obtained meets quality objectives. This is an ongoing

process that continues every day the project is implemented. Routine assessments and communication are required to ensure any problems are quickly identified and resolved.

C1.2 – Response Actions

Despite best preparations, assessments may find situations requiring corrective actions. Small day-to-day level assessment findings are often addressed by the individual doing the assessment in the field or in the lab and are common enough to the process to not necessitate a formal response.

QA staff are aware that a response may be necessary (many of these will result in changes to the analytical reporting via data qualifiers and comments) if any of the following occur:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or relative percent difference between duplicates
- There are unusual changes in detection limits
- Deficiencies are detected by the laboratory, Project Coordinator, and Project QA Officer
- Inquiries concerning data quality are received

Lab corrective actions will follow regular laboratory procedures and SOPs. Any lab corrective action with the potential to affect data quality will be communicated within 24 hours to the Project Coordinator. The laboratory will evaluate if data requires any additional qualifiers and/or if it is usable for its originally intended purpose.

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system will be:

- Checking the predetermined limits for data acceptability beyond which corrective action is required
- Identifying and defining problems
- Assigning responsibility for investigating the problem
- Investigating and determining the cause of the problem
- Determination of a corrective action to eliminate the problem (this may include reanalysis or resampling and analyses)
- Assigning and accepting responsibility for implementing the corrective action
- Implementing the corrective action and evaluating the effectiveness
- Verifying that the corrective action has eliminated the problem
- Documenting the corrective action taken

Field corrective actions may include site access issues or sampling tap access or cross contamination concerns. The need for correcting any of these issues will be minimized to the best of the field staff's ability with ample planning and preparation. Any issues encountered should be discussed with the Project Coordinator.

C1.3 – Reporting and Resolution of Issues

Any findings of practice or procedure that do not conform to the written QAPP will be corrected as soon as possible. Broadbent Project Coordinator and Project QA Officer will be notified regarding deviations.

C1.4 – Data Completeness

Overall success of the project will be determined by the described sampling resulting in successful useable results. Potential data gaps will be monitored as the project progresses, and the schedule will be revised to fill these gaps where they are determined to be significant or to potentially impact the fulfillment of project objectives.

C2 – Reports to Management

Broadbent staff shall be in continuous contact with their immediate supervisor or the Project Coordinator. Reports will include, but not be limited to sample schedules, summaries of activities performed, technical support, etc.

C2.1 –Sample Results

Laboratories will report the compounds identified in the methods as determined by sample source. (Appendix B). Sampling results shall be reported in ng/L. All analytical laboratory reports shall only report on the compounds identified in the methods as determined by sample source 25 analytes listed in Appendix B. Laboratory reports will be sent to the Project Coordinator. The Project Coordinator will notify the NDEP of the results, along with recommendations.

NDEP and the Project Coordinator will determine the appropriate response and will document decisions to proceed.

D1/D2 – Data Review, Verification and Validation Methods

The analytical data generated during this project must be of sufficient quality to decide whether a facility/site shows levels US EPA Method specific analytes (Appendix B). To ensure that this objective is achieved, Broadbent will implement and adhere to the following requirements, data verification and validation activities:

- The laboratories shall adhere to quality control measures as stated in Method 533, Method 537.1, or proposed Method 1633.
- At the discretion of NDEP, facilities/sites that exhibit PFAS detections may be resampled and reanalyzed by Broadbent (as described in Section B1.3) to verify the detection. Resampling will significantly reduce the potential for analytical false positives.

The Project QA Officer will evaluate all components of the sampling process and analytical reports to determine whether the data quality objective has been met and that data are appropriate as a basis for recommendations regarding the presence of PFAS in facilities/sites. This person will convey this information to the rest of the team.

D1.1 – Precision

Precision of field sampling procedures will be evaluated by assessing the RPD data from field duplicate samples. Analytical precision will be evaluated by assessing the RPD data from either duplicate spiked sample analyses or duplicate LCS analyses. The RPD between two measurements is calculated using the following simplified formula:

Where:

$$\text{RPD} = \frac{|R1-R2|}{(R1+R2)/2} \times 100\%$$

R_1 = Value of first result

R_2 = Value of second result

RPD data will provide the means to evaluate the overall variability attributable to the sampling procedure, sample matrix, and laboratory procedures. It should be noted that the RPD of two measurements can be very high when the concentrations approach the quantitation limit of an analysis.

D1.2 – Accuracy/Bias

The data from method blank samples, surrogate compound spikes, LCS, and MS will be used to determine accuracy and potential bias of the sample data.

The data from method blank samples provide an indication of laboratory contamination that may result in bias of sample data. Sample data associated with method blank contamination will have been identified during the data validation process. Sample data associated with method blank contamination are evaluated during the data validation procedure to determine if analytes detected in samples associated with contaminated method blanks are "real" or are impacted by laboratory contamination. The procedure for this evaluation involves comparing the concentration of the analyte in the sample to the concentration in the method blank sample taking into account adjustments for sample preparation and dilution factors. In general, the sample data are qualified as non-detect "U" if both the sample and blank concentrations are less than the reporting limit or less than 2x the reporting limit for common laboratory organic contaminants (acetone, 2-butanone and methylene chloride). The "U" qualifier indicates that the result is a laboratory artifact based on the method blank contamination.

The data from equipment and field blank samples provide an indication of field conditions that may result in bias of sample data. Sample data associated with contaminated equipment blank samples will have been identified during the data validation process. The evaluation procedure and qualification of sample data associated with equipment contamination are performed in a similar manner as the evaluation procedure for method blank sample contamination.

MS sample data provide information regarding the accuracy/bias of the analytical methods relative to the sample matrix. MS samples are field samples that have been fortified with target analytes prior to sample preparation and analysis. The percent recovery data provide an indication of the effect that the sample matrix may have on the preparation and analysis procedure. Sample data exhibiting matrix effects will have been identified during the data verification/validation process.

Analytical accuracy/bias will be determined by evaluating the percent recovery data of LCS. LCS are artificial samples prepared in the laboratory using a blank matrix fortified with analytes from a standard

reference material that is independent of the calibration standards. LCS are prepared and analyzed in the same manner as the field samples. The percent recovery data from LCS analyses will provide an indication of the accuracy and bias of the analytical method for each analyte or analyte group.

Percent recovery is calculated using the following formula:

$$\%R = \frac{SSR - SR}{SA} X\ 100$$

Where:

SSR = Spiked Sample Result

SR = Sample Result or Background

SA = Spike Added

D3 – Reconciliation with User Requirements

As a Nevada certified laboratory, the laboratory is required to afford their clients cooperation to clarify the client's requests and to monitor the laboratory performance in relation to the work performed. Additionally, the laboratory shall have a policy and procedures that shall be implemented when any aspect of its environmental testing work, or the results of this work, do not conform to its own procedures or the agreed requirements of the client. The policy and procedures shall ensure that:

a) the responsibilities and authorities for the management of nonconforming work are designated and actions (including halting of work and withholding of test reports, as necessary) are defined and taken when nonconforming work is identified;
b) an evaluation of the significance of the nonconforming work is made;
c) corrective actions are taken immediately, together with any decision about the acceptability of the nonconforming work;
d) where the data quality is or may be impacted, the client is notified;
e) the responsibility for authorizing the resumption of work is defined.

Appendix A

Standard Operating Procedure for PFAS Sample Collection

1. Introduction

This procedure is intended for personnel authorized to collect samples in support of this QAPP. The samples collected are to identify any levels of PFAS (per- and polyfluoroalkyl substances). The most extensively produced and studied of these chemicals are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS).

This sampling effort is not being carried out under any federal regulation.

Broadbent will coordinate with the facility/site, to identify the sampling locations and number of samples needed. This project requires a one-time sampling event. However, Nevada Division of Environmental Protection (NDEP) may request follow up sampling if detections exceed the Health Advisory Limit (HAL). If sampling must deviate from this guidance, the sampler will contact the Project Coordinator for approval and record detailed notes of any deviation and approval in their field forms.

Broadbent will arrange for the sample collectors to receive sample bottles, and to ship the samples to the lab for analysis. See below for shipping guidance.

2. Definitions

°C	Degrees Celsius
COC	Chain of Custody
FRB	Field Reagent Blank
HAL	Health Advisory Limit
HDPE	High Density Polyethylene
mL	milliliter
NDEP	Nevada Division of Environmental Protection
PFAS	per- and polyfluoroalkyl substances
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PVC	Polyvinyl Chloride
USEPA	United States Environmental Protection Agency

3. Safety Requirements

A health and safety plan should be prepared prior to commencing all field work on site and should be regularly reviewed and updated throughout the project as changes in conditions or work methods occur.

Reference should be made to safety requirements and considerations described in specific sampling procedures. The following provides a brief summary of some typical safety issues associated with water sampling.

Weather

Consider the effect that adverse weather conditions may have on the safety of the sampling process.

Sampling from Boats

Stability is an important property of any boat used for sampling purposes. Precautions should be taken in relation to other boats or ships, e.g. the correct signal flags should be flown, to indicate the nature of the work being undertaken. Safety flares, emergency beacons and communication devices should be considered. Lifejackets should always be worn when sampling from boats. Boats should be capable of reaching all sampling positions within the time limits of the survey in suitable weather conditions.

4. Sampling Equipment and Procedure

a. Drinking Water

1. Sampling Equipment
    a. You will receive two 250-mL polypropylene sample bottles in which the samples must be collected. One bottle will contain ammonium acetate and one bottle will contain Trizma which helps chemically preserve the sample.
    b. You will also receive Field Reagent Blanks (FRB), which are sample bottles filled with PFAS-free water (verified by the laboratory) and preservatives, as well as an empty sample bottle. These are to be used as outlined in the sample procedure below.
    c. You will receive a cooler in which to store the samples for shipping back to the lab.
    d. The sampler will need to procure wet ice for storing the samples inside the cooler.
    e. Secure shut the cooler with packing tape before you ship it out.
2. Minimize use of the following products on the day of the sample event, preferably **24 hours prior to the event**:
    a. Cosmetics, moisturizers, sun-blocks, insect repellants, fragrances, creams, or other personal care products (including hair products). Exceptions: Products that are known to be 100% natural.
    b. Other items that are likely to contain PFAS and to be avoided include:
        i. Paper packaging for food or fast food.
        ii. New or unwashed clothing.
        iii. Clothing washed with fabric softeners or dried with anti-static sheets.
        iv. Synthetic water-resistant/or stain-resistant materials (such as waterproof clothing and shoes such as Gore-Tex), waterproof or coated Tyvek® material (special attention to boots).
        v. Teflon® and other fluoropolymer-containing materials (e.g., polyvinylidene fluoride [PVDF], Kynar®, Neoflon®, Tefzel®).
        vi. Waterproof/treated paper on field notebooks.
        vii. Waterproof markers (such as Sharpie®, etc.).

viii. Chemical or blue ice, which may contain PFAS and may not reduce and/or maintain the temperature of the samples adequately.
ix. Avoid sampling in the rain if possible (if necessary, use vinyl or polyvinyl chloride [PVC] rain gear).

3. Sampling Teams
   a. **Two-person sampling teams are highly recommended**. Distributing the workload to ensure attention to sampling procedures is easier with a two-person team.
   b. When sampling for PFAS, a two-person team allows one person to be a dedicated "sample" handler, and the other person the dedicated "document" handler. One team member obtains the samples, and the other team member records the samples on the COC form with the sample collection information. If only one person is conducting the sampling, ensure care is taken to properly record all samples on the COC, and follow all the precautions noted in this guidance.

4. Sampling Procedure
   a. The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.
   b. Bottle labels and the COC should be completed before sample collection with the exception of the sample time.
   c. The sample tap should be flushed for a minimum of 5 minutes to ensure the impact of local sources of PFAS cross-contamination, such as Teflon® tape and valve seats, are minimized. The presence of Teflon® and other fluoropolymer-containing materials should be clearly noted in the field notebook. **Don't flush the tap while collecting the Field Reagent Blank (FRB).** Be sure to remove aerators, screens, washers, hoses, and water filters from the tap prior to flushing.
   d. FRB Procedure
   i) Collect the FRB prior to the collection of the Field Sample.
      ii) At the sampling site, the sample personnel must open the empty FRB sample bottle, pour the pre-preserved PFAS-free reagent water into the sample bottle, and seal and label this bottle as the FRB. Record the FRB identification number on the COC form.
      iii) The FRB is shipped back to the laboratory along with the site samples. The empty container that the field reagent water was poured out of must also be shipped back to the laboratory in the same shipment.
   e. Uncap the sample bottle. **Do not place the bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.**
   f. Fill sample bottles, taking care not to flush out the sample preservation reagent. Samples do not need to be collected headspace free, but a volume of 250 mL is necessary for the sample analysis. Do not overfill.
   g. After collecting the sample, cap the bottle and agitate by hand until preservative is dissolved. Keep the sample sealed from time of collection until extraction.

b. Surface Water Samples

1. Sampling Equipment
    a. You will receive 500-mL polypropylene sample bottles in which the samples must be collected.
    b. You will receive a cooler in which to store the samples for shipping back to the lab.
    c. The sampler will need to procure wet ice for storing the samples inside the cooler.
    d. Secure shut the cooler with packing tape before you ship it out.
2. Minimize use of the following products on the day of the sample event, preferably **24 hours prior to the event**:
    a. Cosmetics, moisturizers, sun-blocks, insect repellants, fragrances, creams, or other personal care products (including hair products). Exceptions: Products that are known to be 100% natural.
    b. Other items that are likely to contain PFAS and to be avoided include:
        x. Paper packaging for food or fast food.
        xi. New or unwashed clothing.
        xii. Clothing washed with fabric softeners or dried with anti-static sheets.
        xiii. Synthetic water-resistant/or stain-resistant materials (such as waterproof clothing and shoes such as Gore-Tex), waterproof or coated Tyvek® material (special attention to boots).
        xiv. Teflon® and other fluoropolymer-containing materials (e.g., polyvinylidene fluoride [PVDF], Kynar®, Neoflon®, Tefzel®).
        xv. Waterproof/treated paper on field notebooks.
        xvi. Waterproof markers (such as Sharpie®, etc.).
        xvii. Chemical or blue ice, which may contain PFAS and may not reduce and/or maintain the temperature of the samples adequately.
        xviii. Avoid sampling in the rain if possible (if necessary, use vinyl or polyvinyl chloride [PVC] rain gear).

3. Sampling Teams
    a. **Two-person sampling teams are highly recommended**. Distributing the workload to ensure attention to sampling procedures is easier with a two-person team.
    b. When sampling for PFAS, a two-person team allows one person to be a dedicated “sample” handler, and the other person the dedicated “document” handler. One team member obtains the samples, and the other team member records the samples on the COC form with the sample collection information. If only one person is conducting the sampling, ensure care is taken to properly record all samples on the COC, and follow all the precautions noted in this guidance.

4. Sampling Procedure
    a. The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

b. Bottle labels and the COC should be completed before sample collection with the exception of the sample time.
c. Utilizing a decontaminated sampling pole, attach the sample bottle to the pole.
    i) Use only sample collection equipment, tubing beakers, and/or scoop materials that are known to be PFAS-free such as stainless steel, HDPE, PVC, polypropylene, acetate, or silicone.
    ii) Equipment rinsate blank samples should be collected to make certain the sampler is PFAS-free.
d. Uncap the sample bottle. **Do not place the bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.**
e. Place the container directly into the water body, open end vertically down and submerge to a depth of six inches or the mid-depth of the waterbody. Fill with an arc motion with the bottle mouth facing upstream. Avoid collecting surface films or agitating and collecting sediment.
f. Fill sample bottles to the shoulder. Samples do not need to be collected headspace free, but a volume of 500 mL is necessary for the sample analysis. Do not overfill.
g. Collect at least two aliquots of all aqueous samples to allow sufficient volume for determination of percent solids and for pre-screening analysis. The second aliquot may be collected in a smaller sample container (e.g. 250-mL or 125-mL containers).
h. After collecting the sample, cap the bottle. Keep the sample sealed from time of collection until extraction.

c. Treated Wastewater Samples

1. Sampling Equipment
    a. You will receive 500-mL polypropylene sample bottles in which the samples must be collected.
    b. You will receive a cooler in which to store the samples for shipping back to the lab.
    c. The sampler will need to procure wet ice for storing the samples inside the cooler.
    d. Secure shut the cooler with packing tape before you ship it out.
2. Minimize use of the following products on the day of the sample event, preferably **24 hours prior to the event**:
    a. Cosmetics, moisturizers, sun-blocks, insect repellants, fragrances, creams, or other personal care products (including hair products). Exceptions: Products that are known to be 100% natural.
    b. Other items that are likely to contain PFAS and to be avoided include:
        xix. Paper packaging for food or fast food.
        xx. New or unwashed clothing.
        xxi. Clothing washed with fabric softeners or dried with anti-static sheets.
        xxii. Synthetic water-resistant/or stain-resistant materials (such as waterproof clothing and shoes such as Gore-Tex), waterproof or coated Tyvek® material (special attention to boots).
        xxiii. Teflon® and other fluoropolymer-containing materials (e.g., polyvinylidene fluoride [PVDF], Kynar®, Neoflon®, Tefzel®).
        xxiv. Waterproof/treated paper on field notebooks.

xxv. Waterproof markers (such as Sharpie®, etc.).
xxvi. Chemical or blue ice, which may contain PFAS and may not reduce and/or maintain the temperature of the samples adequately.
xxvii. Avoid sampling in the rain if possible (if necessary, use vinyl or polyvinyl chloride [PVC] rain gear).

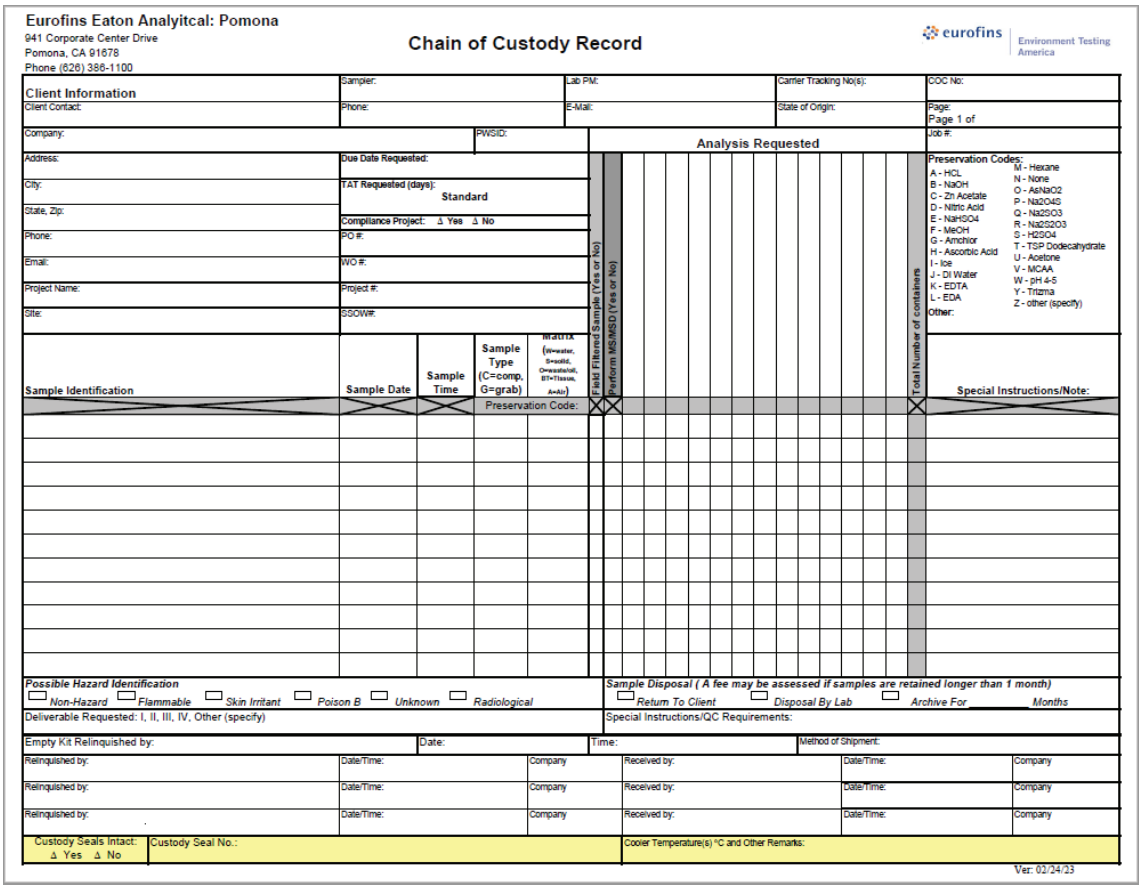
3. Sampling Teams
   a. **Two-person sampling teams are highly recommended**. Distributing the workload to ensure attention to sampling procedures is easier with a two-person team.
   b. When sampling for PFAS, a two-person team allows one person to be a dedicated "sample" handler, and the other person the dedicated "document" handler. One team member obtains the samples, and the other team member records the samples on the COC form with the sample collection information. If only one person is conducting the sampling, ensure care is taken to properly record all samples on the COC, and follow all the precautions noted in this guidance.

4. Sampling Procedure
   a. The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.
   b. Bottle labels and the COC should be completed before sample collection with the exception of the sample time.
   c. Proceed to the treated wastewater effluent sample port identified by the facility operator.
      i) If permissible by the facility, the sample port should be flushed for a minimum of 5 minutes to ensure the impact of local sources of PFAS cross-contamination, such as Teflon® tape and valve seats, are minimized.
      ii) If flushing is not permissible, collect the sample directly for the sample port.
      iii) The presence of Teflon® and other fluoropolymer-containing materials should be clearly noted in the field notebook.
   d. If a sample port is not present and a sample can be collected safely from a discharge outfall, attach the sample bottle to a decontaminated sampling pole.
      i) Use only sample collection equipment, tubing beakers, and/or scoop materials that are known to be PFAS-free such as stainless steel, HDPE, PVC, polypropylene, acetate, or silicone.
      ii) Equipment rinsate blank samples should be collected to make certain the sampler is PFAS-free.
   e. Uncap the sample bottle. **Do not place the bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.**
   f. Place the container directly into the water body, open end vertically down and submerge to a depth of six inches or the mid-depth of the waterbody. Fill with an arc motion with the bottle mouth facing upstream. Avoid collecting surface films or agitating and collecting sediment.

g. Fill sample bottles to the shoulder. Samples do not need to be collected headspace free, but a volume of 500 mL is necessary for the sample analysis. Do not overfill.
h. Collect at least two aliquots of all aqueous samples to allow sufficient volume for determination of percent solids and for pre-screening analysis. The second aliquot may be collected in a smaller sample container (e.g. 250-mL or 125-mL containers).
i. After collecting the sample, cap the bottle. Keep the sample sealed from time of collection until extraction.

5. Sample Shipment and Storage

1. Sampling must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection.
   a. All samples will be packed according to the following guidelines and then shipped over-night to the designated lab.
   b. After sampling, insert sample containers into Ziploc bags. Tie a knot at the top of the inner bag around the sample containers.
   c. Ice should not be placed outside of the cooler liner or the cooler may leak as the ice melts. As an alternative to a cooler liner, ice may be contained in double-plastic bags (e.g., 1- or 2-gallon Ziploc bags).
   d. Place completed COC in a Ziploc bag and place them in the cooler on top of the outer liner.
2. Chain of Custody and Sampling Form.



Eurofins Eaton Analyitcal: Pomona
941 Corporate Center Drive
Pomona, CA 91678
Phone (626) 386-1100

Chain of Custody Record

eurofins | Environment Testing America

Client Information	Sampler:	Lab PM:	Carrier Tracking No(s):	COC No:
Client Contact:	Phone:	E-Mail:	State of Origin:	Page: Page 1 of
Company:	PWSID:			Job #:
Address:	Due Date Requested:	Analysis Requested		Preservation Codes: A - HCL, B - NaOH, C - Zn Acetate, D - Nitric Acid, E - NaHSO4, F - MeOH, G - Amchlor, H - Ascorbic Acid, I - Ice, J - DI Water, K - EDTA, L - EDA, Other: / M - Hexane, N - None, O - AsNaO2, P - Na2O4S, Q - Na2SO3, R - Na2S2O3, S - H2SO4, T - TSP Dodecahydrate, U - Acetone, V - MCAA, W - pH 4-5, Y - Trizma, Z - other (specify)
City:	TAT Requested (days): Standard			
State, Zip:	Compliance Project: Δ Yes Δ No			
Phone:	PO #:			
Email:	WO #:			
Project Name:	Project #:			
Site:	SSOW#:			

Sample Identification	Sample Date	Sample Time	Sample Type (C=comp, G=grab)	Matrix (W=water, S=solid, O=waste/oil, BT=Tissue, A=Air)	Field Filtered Sample (Yes or No)	Perform MS/MSD (Yes or No)	Total Number of containers	Special Instructions/Note:
			Preservation Code:					

Possible Hazard Identification: ☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown ☐ Radiological
Sample Disposal (A fee may be assessed if samples are retained longer than 1 month): ☐ Return To Client ☐ Disposal By Lab ☐ Archive For _____ Months
Deliverable Requested: I, II, III, IV, Other (specify)
Special Instructions/QC Requirements:

Empty Kit Relinquished by:	Date:	Time:	Method of Shipment:

Relinquished by:	Date/Time:	Company	Received by:	Date/Time:	Company
Relinquished by:	Date/Time:	Company	Received by:	Date/Time:	Company
Relinquished by:	Date/Time:	Company	Received by:	Date/Time:	Company

Custody Seals Intact: Δ Yes Δ No | Custody Seal No.: | Cooler Temperature(s) °C and Other Remarks:

Ver: 02/24/23

Figure 1 Chain of Custody (COC) form

Sample Collection Form

Sample Type: Drinking Water / Wastewater / Surface Water (Circle one)

Project: NDEP PFAS Sampling
Client: NDEP
Project #: 23-02-119

Date:

BROADBENT

Sample ID	Sample Time 24hr : min	Temperature °C	Conductivity mS/cm	pH SU	Turbidity NTU	

Sample Collected: YES / NO (circle one)	Sample Location (Decimal degrees NAD 83)	
Drinking Water Sample Facility Name / Outfall Sample Outfall Number / Surface Water Sample Monitoring Station Code	Latitude	
	Longitude	
	GPS Accuracy (ft)	
Comments:		
Sampler:		

Analyses Requested (select all that apply):		Number of Sample Containers	Quality Control Samples (List Duplicate or MS/MSD)
	Method 537.1		
	Method 533		
	Method 1633		

Version 09/13/2023

Figure 2 Sampling Form

3. On the Chain of Custody, write the following information:
   a. The sampler's (your) name, position, signature and date.
   b. Date (MM/DD/YYYY) and time (24 hour time) that each sample is being taken
   c. If applicable, write comments, including any potential abnormalities during sampling procedures. Examples: water pressure was high causing water to splash out of bottle, bottle was too big to fit under drinking fountain and water spilled, etc.
4. On the sampling bottle, write the sample ID, your initials, date and time of the sample, and general location. Write the method appropriate preservative in preservative box, and "PFAS" in analysis. See example in Figure 3.

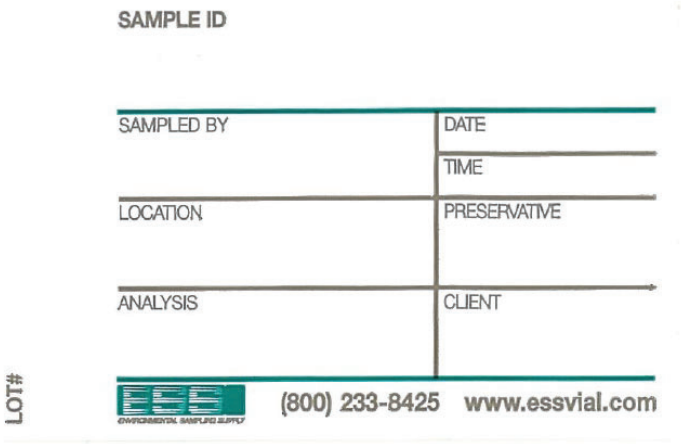


Figure 3 Example Sample Bottle Label

The chain of custody seal is a sticker that can be put over the lid of the cooler to show that nothing has been opened since the sample was taken. Please sign the seal and print the sampler's (your) name and date.

5. Mail the cooler back to the designated lab in accordance to the shipping instructions. Include the chain of custody form.

Samples must be received by the lab within 48 hours of collection, so please ensure you return the samples promptly to:

US EPA Method 533 and 537.1:

Samples Receiving
Eurofins Eaton Analytical
941 Corporate Center Dr.
Pomona, CA 91678

US EPA Proposed Method 1633:

Samples Receiving
Eurofins TestAmerica
880 Riverside Pkwy.
West Sacramento CA 95605

6. Scan and email a copy of the completed Chain of Custody form and Sampling form to the Project Coordinator.
7. Call or email the laboratory to make sure that the lab receives the samples.

Eurofins - Pomona	Phone: 626-386-1138 Email: eduardo.rodriguez@et.eurofins.com

Results from this monitoring effort and information about PFAS will be provided to you as soon as practical.

6. References

Method 533: Determination of Per- And Polyfluoroalkyl Substances in Drinking water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. United States Environmental Protection Agency. November 2019

Method 537.1: Determination of Selected Per- And Polyfluorinated Alkyl Substances in Drinking water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. United States Environmental Protection Agency. November 2018

Draft Method 1633: Analysis of Per- And Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. United States Environmental Protection Agency. November 2019

General PFAS Sampling Guidance. Michigan Department of Environmental Quality. October 2018.

Appendix B

List of EPA Method 533 PFAS analytes

Target Analyte Name	Abbreviation	Reg # (CAS)
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoroundecanoic acid	PFUnA	2058-94-8
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Perfluorobutanoic acid	PFBA	375-22-4
1H, 1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
1H, 1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
1H, 1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluoropentanesulfonic acid	PFPeS	2706-91-4

List of EPA Method 537.1 PFAS analytes

Target Analyte Name	Abbreviation	Reg # (CAS)
N-ethyl Perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl Perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8
Hexafluoropropylene oxide dimer acid	HFPO-DA / GenX	13252-13-6[a]
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4

List of Proposed EPA Method 1633 PFAS analytes

Target Analyte Name	Abbreviation	CAS Number
Ether sulfonic acids		
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7
Fluorotelomer carboxylic acids		
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	5:3FTCA	914637-49-3
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4
EIS Compounds		
Perfluoro-n-[^{13}C$_4$]butanoic acid	^{13}C4-PFBA	N/A
Perfluoro-n-[^{13}C$_5$]pentanoic acid	^{13}C5-PFPeA	
Perfluoro-n-[1,2,3,4,6-^{13}C$_5$]hexanoic acid	^{13}C5-PFHxA	
Perfluoro-n-[1,2,3,4-^{13}C$_4$]heptanoic acid	^{13}C4-PFHpA	
Perfluoro-n-[^{13}C$_8$]octanoic acid	^{13}C8-PFOA	
Perfluoro-n-[^{13}C$_9$]nonanoic acid	^{13}C9-PFNA	
Perfluoro-n-[1,2,3,4,5,6-^{13}C$_6$]decanoic acid	^{13}C6-PFDA	
Perfluoro-n-[1,2,3,4,5,6,7-^{13}C$_7$]undecanoic acid	^{13}C7-PFUnA	
Perfluoro-n-[1,2-^{13}C$_2$]dodecanoic acid	^{13}C2-PFDoA	
Perfluoro-n-[1,2-^{13}C$_2$]tetradecanoic acid	^{13}C2-PFTeDA	
Perfluoro-1-[2,3,4-^{13}C$_3$]butanesulfonic acid	^{13}C3-PFBS	
Perfluoro-1-[1,2,3-^{13}C$_3$]hexanesulfonic acid	^{13}C3-PFHxS	
Perfluoro-1-[^{13}C$_8$]octanesulfonic acid	^{13}C8-PFOS	
Perfluoro-1-[^{13}C$_8$]octanesulfonamide	^{13}C8-PFOSA	
N-methyl-d$_3$-perfluoro-1-octanesulfonamidoacetic acid	D3-NMeFOSAA	
N-ethyl-d$_5$-perfluoro-1-octanesulfonamidoacetic acid	D5-NEtFOSAA	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-[1,2-^{13}C$_2$]hexan sulfonic acid	^{13}C2-4:2FTS	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-[1,2-^{13}C$_2$]octanesulfonic acid	^{13}C2-6:2FTS	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-[1,2-^{13}C$_2$]decanesulfonic acid	^{13}C2-8:2FTS	
Tetrafluoro-2-heptafluoropropoxy-^{13}C$_3$-propanoic acid	^{13}C3-HFPO-DA	
N-methyl-d$_7$-perfluorooctanesulfonamidoethanol	D7-NMeFOSE	
N-ethyl-d$_9$-perfluorooctanesulfonamidoethanol	D9-NEtFOSE	
N-ethyl-d$_5$-perfluoro-1-octanesulfonamide	D5-NEtFOSA	

N-methyl-d3 -perfluoro-1-octanesulfonamide	D3 -NMeFOSA	
NIS Compounds		N/A
Perfluoro-n-[2,3,4-$^{13}C_3$]butanoic acid	$^{13}C3$ -PFBA	
Perfluoro-n-[1,2,3,4-$^{13}C4$]octanoic acid	$^{13}C4$ -PFOA	
Perfluoro-n-[1,2-$^{13}C2$]decanoic acid	$^{13}C2$ -PFDA	
Perfluoro-n-[1,2,3,4-$^{13}C4$]octanesulfonic acid	$^{13}C4$ -PFOS	
Perfluoro-n-[1,2,3,4,5-$^{13}C5$] nonanoic acid	$^{13}C5$ -PFNA	
Perfluoro-n-[1,2-$^{13}C2$]hexanoic acid	$^{13}C2$ -PFHxA	
Perfluoro-1-hexane[$^{18}O2$]sulfonic acid	$^{18}O2$ -PFHxS	

Appendix C

Sample Locations

Table 1: Priority Sample Sites – Drinking Water Protection Areas, Water System Sources

The following drinking water protection areas received the highest sample priority scores. The table below shows the information for the water system source (well, spring, or intake) within the drinking water protection area. Higher scores indicate a higher sample priority, based upon the presence of potential PFAS contributors and/or PFAS detections within the drinking water protection area. This list includes sites that received a score of 5 or higher.

Map ID	Sample Priority Score	System Name	Facility Name	County Served	Water Type
1	**12**	TRUCKEE MEADOWS WATER AUTHORITY	PEZZI WELL	WASHOE	GROUNDWATER
2	**12**	TRUCKEE MEADOWS WATER AUTHORITY	POPLAR ST WELL 1	WASHOE	GROUNDWATER
3	**12**	TRUCKEE MEADOWS WATER AUTHORITY	CORBETT WELL	WASHOE	GROUNDWATER
4	**12**	TRUCKEE MEADOWS WATER AUTHORITY	TERMINAL WAY WELL	WASHOE	GROUNDWATER
5	**12**	TRUCKEE MEADOWS WATER AUTHORITY	MILL ST WELL	WASHOE	GROUNDWATER
6	**11**	TRUCKEE MEADOWS WATER AUTHORITY	GLENDALE RAW WATER INTAKE	WASHOE	SURFACE WATER
7	**11**	TRUCKEE MEADOWS WATER AUTHORITY	GREG ST WELL	WASHOE	GROUNDWATER
8	**11**	TRUCKEE MEADOWS WATER AUTHORITY	POPLAR ST WELL 2	WASHOE	GROUNDWATER
9	**11**	TRUCKEE MEADOWS WATER AUTHORITY	S TWENTYFIRST ST WELL	WASHOE	GROUNDWATER
10	**11**	TRUCKEE MEADOWS WATER AUTHORITY	GALLETTI WELL	WASHOE	GROUNDWATER
11	**9**	CHUCK LENZIE GENERATING STATION	CHUCK WELL WS-1	CLARK	GROUNDWATER
12	**9**	NELLIS AIR FORCE BASE	AREA 1 WELL 7 489 NON-POTABLE EMERGENCY	CLARK	GROUNDWATER
13	**9**	NELLIS AIR FORCE BASE	AREA 1 WELL 14 NON-POTABLE EMERGENCY	CLARK	GROUNDWATER
14	**9**	NELLIS AIR FORCE BASE	AREA 1 WELL 11 NON-POTABLE EMERGENCY	CLARK	GROUNDWATER
15	**9**	EP MINERALS LLC CLARK	WELL 1	STOREY	GROUNDWATER
16	**8**	ALAMO SEWER AND WATER GID	SANDHILL WELL	LINCOLN	GROUNDWATER
17	**8**	TRUCKEE MEADOWS WATER AUTHORITY	SPARKS AVE WELL	WASHOE	GROUNDWATER
18	**8**	TRUCKEE MEADOWS WATER AUTHORITY	VIEW ST WELL	WASHOE	GROUNDWATER
19	**8**	CREECH AIR FORCE BASE	WELL 62-5	CLARK	GROUNDWATER
20	**8**	CHUCK LENZIE GENERATING STATION	CHUCK WELL WS-3	CLARK	GROUNDWATER
21	**8**	NELLIS AIR FORCE BASE	AREA 1 WELL 12 NON-POTABLE EMERGENCY	CLARK	GROUNDWATER
22	**8**	CANYON GID	WELL 1	STOREY	GROUNDWATER
23	**7**	DENIO JUNCTION	WELL 1	HUMBOLDT	GROUNDWATER
24	**7**	CARSON CITY PUBLIC WORKS	WELL 33 BRUNSWICK	CARSON CITY	GROUNDWATER
25	**7**	CRESCENT VALLEY WATER SYSTEM	WELL 4	EUREKA	GROUNDWATER
26	**7**	INDIAN SPRINGS WATER CO INC	WELL 1	CLARK	GROUNDWATER
27	**7**	JACKPOT WATER SYSTEM	GOLF COURSE WELL	ELKO	GROUNDWATER
28	**7**	LUNA VISTA	LAKEWAY RNT WELL	CLARK	GROUNDWATER
29	**7**	NORTH LAS VEGAS UTILITIES	WELL ROBINSON	CLARK	GROUNDWATER
30	**7**	TRUCKEE MEADOWS WATER AUTHORITY	CHALK BLUFF RAW WATER INTAKE	WASHOE	SURFACE WATER
31	**7**	TRUCKEE MEADOWS WATER AUTHORITY	HIDDEN VALLEY WELL 5	WASHOE	GROUNDWATER
32	**7**	SILVER SPRINGS MUTUAL WATER COMPANY	WELL 4 IDAHO ST	LYON	GROUNDWATER
33	**7**	SILVER SPRINGS MUTUAL WATER COMPANY	DEODAR REPLACEMENT WELL	LYON	GROUNDWATER
34	**7**	HAWTHORNE ARMY DEPOT	BLACK BEAUTY RESERVOIR INTAKES	MINERAL	SURFACE WATER
35	**7**	HAWTHORNE ARMY DEPOT	WELL 4 W02	MINERAL	GROUNDWATER
36	**7**	HAWTHORNE ARMY DEPOT	WELL 11 W03	MINERAL	GROUNDWATER
37	**7**	TOLICHA PEAK ELECTRONIC COMBAT RANGE	WELL 1	NYE	GROUNDWATER

38	**7**	BALD MOUNTAIN MINE	WELL	WHITE PINE	GROUNDWATER
39	**7**	TROPICANA RESORT AND CASINO	TROP WELL 3 EAST	CLARK	GROUNDWATER
40	**7**	TROPICANA RESORT AND CASINO	TROP WELL 4 SOUTH	CLARK	GROUNDWATER
41	**7**	CREECH AIR FORCE BASE	WELL 106-3	CLARK	GROUNDWATER
42	**7**	CREECH AIR FORCE BASE	WELL 106-4	CLARK	GROUNDWATER
43	**7**	CEDAR PASS WATER SYSTEM	WELL	NYE	GROUNDWATER
44	**7**	KAPEX WATER SYSTEM CITY OF NLV	WELL 1	CLARK	GROUNDWATER
45	**7**	FIRESIDE INN	WELL	WHITE PINE	GROUNDWATER
46	**7**	CARSON VALLEY WATER SYSTEM	AIRPORT SOUTH WELL	DOUGLAS	GROUNDWATER
47	**7**	NAS CENTROID EW RANGE	CENTROID WELL	CHURCHILL	GROUNDWATER
48	**7**	HOOVER DAM	HOOVER DAM INTAKE ARIZONA TOWER 3	CLARK	SURFACE WATER
49	**7**	TONOPAH TEST RANGE SITE 6	WELL 6	NYE	GROUNDWATER
50	**7**	NELLIS AIR FORCE BASE	AREA 1 WELL 1 NON-POTABLE EMERGENCY	CLARK	GROUNDWATER
51	**7**	NELLIS AIR FORCE BASE	CRAIG RD WELL 2	CLARK	GROUNDWATER
52	**7**	NELLIS AIR FORCE BASE	CRAIG RD WELL 8	CLARK	GROUNDWATER
53	**7**	GOLD COUNTRY ESTATES	DOMESTIC WELL 3	HUMBOLDT	GROUNDWATER
54	**7**	GOLD COUNTRY ESTATES	FIRE WELL 4	HUMBOLDT	GROUNDWATER
55	**7**	TONOPAH TEST RANGE MANCAMP	WELL 3 REPLACEMENT FOR WELL 2	NYE	GROUNDWATER
56	**7**	TONOPAH TEST RANGE AREA 10 INDUSTRIAL	WELL EH 2	NYE	GROUNDWATER
57	**7**	TONOPAH ELECTRONIC COMBAT RANGE O AND M	O AND M WELL	NYE	GROUNDWATER
58	**6**	CARSON CITY PUBLIC WORKS	WELL 40 MORGAN MILL	CARSON CITY	GROUNDWATER
59	**6**	CARSON CITY PUBLIC WORKS	WELL 44 EMPIRE RANCH RD	CARSON CITY	GROUNDWATER
60	**6**	HAWTHORNE UTILITIES	I ST WELL	MINERAL	GROUNDWATER
61	**6**	HAWTHORNE UTILITIES	BABBITT WELL 7	MINERAL	GROUNDWATER
62	**6**	INDIAN SPRINGS WATER CO INC	WELL 2	CLARK	GROUNDWATER
63	**6**	JACKPOT WATER SYSTEM	FIRE HOUSE WELL	ELKO	GROUNDWATER
64	**6**	JACKPOT WATER SYSTEM	CACTUS PETE WELL	ELKO	GROUNDWATER
65	**6**	JACKPOT WATER SYSTEM	PARK WELL	ELKO	GROUNDWATER
66	**6**	JACKPOT WATER SYSTEM	WELL 6	ELKO	GROUNDWATER
67	**6**	LAS VEGAS VALLEY WATER DISTRICT	WELL 45 2300 ZONE	CLARK	GROUNDWATER
68	**6**	EASTLAND HEIGHTS WATER ASSOCIATION	VALLEY WELL	CLARK	GROUNDWATER
69	**6**	HILLCREST MANOR WATER USERS ASSOCIATION	WELL 1B MADRE MESA	CLARK	GROUNDWATER
70	**6**	HILLCREST MANOR WATER USERS ASSOCIATION	WELL 2B SHEILA	CLARK	GROUNDWATER
71	**6**	PANACA FARMSTEAD ASSOCIATION	WELL 3 - EMERGENCY ONLY	LINCOLN	GROUNDWATER
72	**6**	TRUCKEE MEADOWS WATER AUTHORITY	SILVER LAKE REPLACEMENT WELL	WASHOE	GROUNDWATER
73	**6**	TRUCKEE MEADOWS WATER AUTHORITY	SILVER KNOLLS WELL	WASHOE	GROUNDWATER
74	**6**	RIO VISTA MHC LLC	WELL 1 OFFICE	WASHOE	GROUNDWATER
75	**6**	RIO VISTA MHC LLC	WELL 2	WASHOE	GROUNDWATER
76	**6**	SILVER SPRINGS MUTUAL WATER COMPANY	WELL 5 LAKE STREET	LYON	GROUNDWATER
77	**6**	WEED HEIGHTS DEVELOPMENT	WELL 1 TAC WELL	LYON	GROUNDWATER
78	**6**	YERINGTON CITY OF	WELL 3 BROADWAY	LYON	GROUNDWATER

79	6	YERINGTON CITY OF	WELL 6 MOUNTAIN VIEW (REPLACEMENT)	LYON	GROUNDWATER
80	6	YERINGTON CITY OF	NEW CALIFORNIA WELL (REPLACEMENT)	LYON	GROUNDWATER
81	6	WALKER LAKE GID	MALLET WELL	MINERAL	GROUNDWATER
82	6	ELKO CITY OF	WELL 30	ELKO	GROUNDWATER
83	6	ELKO CITY OF	WELL 15	ELKO	GROUNDWATER
84	6	ELKO CITY OF	WELL 18	ELKO	GROUNDWATER
85	6	FALLON NAVAL AIR STATION	WELL 1	CHURCHILL	GROUNDWATER
86	6	FALLON NAVAL AIR STATION	WELL 2	CHURCHILL	GROUNDWATER
87	6	FALLON NAVAL AIR STATION	WELL 3	CHURCHILL	GROUNDWATER
88	6	NEVADA TEST AND TRAINING RANGE SILVER FL	SILVER FLAG WELL 2372	CLARK	GROUNDWATER
89	6	WHISPERING VINE	WELL 1	WASHOE	GROUNDWATER
90	6	JOHNNYS RISTORANTE ITALIANO	WELL 1	WASHOE	GROUNDWATER
91	6	RAPPORT EXECUTIVE RETREAT	WELL 1	LINCOLN	GROUNDWATER
92	6	RAPPORT EXECUTIVE RETREAT	WELL 2	LINCOLN	GROUNDWATER
93	6	LHOIST NORTH AMERICA	WELL 1 NORTH OLD WELL	CLARK	GROUNDWATER
94	6	GREAT BASIN WATER CO SPANISH SPRINGS	WELL SS1A	WASHOE	GROUNDWATER
95	6	PETES TRAILER COURT	WELL 2	ELKO	GROUNDWATER
96	6	TRAVEL CENTERS OF AMERICA NO 181	WELL 1	PERSHING	GROUNDWATER
97	6	CAMP FRIAS FRONTIER	WELL 2	LINCOLN	GROUNDWATER
98	6	NEVADA GOLD MINES GOLD QUARRY	WELL PW12	EUREKA	GROUNDWATER
99	6	HOOVER DAM	HOOVER DAM INTAKE ARIZONA TOWER 6	CLARK	SURFACE WATER
100	6	JERRITT CANYON GOLD JERRITT CANYON MINE	WELL WW7	ELKO	GROUNDWATER
101	6	COEUR ROCHESTER INC	WELL PW-3A	PERSHING	GROUNDWATER
102	6	PEACOX CHARITABLE REMAINDER UNITRUST	WELL 1 MAIN	NYE	GROUNDWATER
103	6	ELY CONSERVATION CAMP NDOC	WELL 1	WHITE PINE	GROUNDWATER
104	6	BIG BEND WATER DISTRICT	COLORADO RIVER INTAKE	CLARK	SURFACE WATER
105	6	NEVADA TEST AND TRAINING RANGE PT BRAVO	POINT BRAVO WELL	CLARK	GROUNDWATER
106	6	CANYON GID	WELL 2	STOREY	GROUNDWATER
107	5	COTTONWOOD MHP	NORTH WELL	CARSON CITY	GROUNDWATER
108	5	COTTONWOOD MHP	MIDDLE WELL	CARSON CITY	GROUNDWATER
109	5	COTTONWOOD MHP	SOUTH WELL	CARSON CITY	GROUNDWATER
110	5	FERNLEY PUBLIC WORKS	WELL 9A	LYON	GROUNDWATER
111	5	FERNLEY PUBLIC WORKS	WELL 9	LYON	GROUNDWATER
112	5	GABBS WATER SYSTEM	WELL 1	NYE	GROUNDWATER
113	5	GABBS WATER SYSTEM	WELL 3	NYE	GROUNDWATER
114	5	TOPAZ LAKE WATER CO INC	WELL 1	DOUGLAS	GROUNDWATER
115	5	TOPAZ LAKE WATER CO INC	WELL 2 - EMERGENCY USE ONLY	DOUGLAS	GROUNDWATER
116	5	TOPAZ LAKE WATER CO INC	WELL 4 PINE NUT WELL	DOUGLAS	GROUNDWATER
117	5	LAS VEGAS VALLEY WATER DISTRICT	WELL 7A CHARLESTON HTS 2168 ZONE	CLARK	GROUNDWATER
118	5	LAS VEGAS VALLEY WATER DISTRICT	WELL 68 CHARLESTON HTS 2168 ZONE	CLARK	GROUNDWATER
119	5	LAS VEGAS VALLEY WATER DISTRICT	WELL 81 CHARLESTON HTS 2168 ZONE	CLARK	GROUNDWATER

120	5	LAS VEGAS VALLEY WATER DISTRICT	WELL 82 CHARLESTON HTS 2168 ZONE	CLARK	GROUNDWATER
121	5	LAS VEGAS VALLEY WATER DISTRICT	WELL 90 2635 ZONE	CLARK	GROUNDWATER
122	5	VIRGIN VALLEY WATER DISTRICT	WELL 27B	CLARK	GROUNDWATER
123	5	TOWN OF MINDEN	WELL 4 1769 IRONWOOD DR	DOUGLAS	GROUNDWATER
124	5	TRUCKEE MEADOWS WATER AUTHORITY	SWOPE WELL	WASHOE	GROUNDWATER
125	5	TRUCKEE MEADOWS WATER AUTHORITY	INNOVATION WELL	WASHOE	GROUNDWATER
126	5	WELLS MUNICIPAL WATER DEPARTMENT	HEAVY INDUSTRIAL PARK WELL	ELKO	GROUNDWATER
127	5	WALKER LAKE GID	BIGHORN WELL	MINERAL	GROUNDWATER
128	5	ELKO CITY OF	WELL 20	ELKO	GROUNDWATER
129	5	LEE CANYON SKI AREA	WELL 1	CLARK	GROUNDWATER
130	5	LEE CANYON SKI AREA	WELL 2	CLARK	GROUNDWATER
131	5	CERTAIN TEED GYPSUM	SOUTH WELL	CLARK	GROUNDWATER
132	5	CERTAIN TEED GYPSUM	NORTH WELL	CLARK	GROUNDWATER
133	5	RENO SAHARA TRAILER PARK	WELL 1	WASHOE	GROUNDWATER
134	5	RENO SAHARA TRAILER PARK	WELL 2	WASHOE	GROUNDWATER
135	5	MOUNT ROSE BOWL PROPERTY OWNERS WATER CO	WELL 1	WASHOE	GROUNDWATER
136	5	MT ROSE SKI TAHOE	SPRING	WASHOE	GROUNDWATER
137	5	SKY TAVERN	SPRING	WASHOE	GROUNDWATER
138	5	SLIDE MOUNTAIN SKI AREA	BRUCES SPRING	WASHOE	GROUNDWATER
139	5	SLIDE MOUNTAIN SKI AREA	WINTERS SPRING	WASHOE	GROUNDWATER
140	5	SLIDE MOUNTAIN SKI AREA	ZEPHER SPRING	WASHOE	GROUNDWATER
141	5	WILLIAMS RIDGE TECH PARK	WELL 1	DOUGLAS	GROUNDWATER
142	5	LONGSTREET INN AND CASINO	WELL 2	NYE	GROUNDWATER
143	5	MARS PETCARE US INC	WELL 1	STOREY	GROUNDWATER
144	5	FRANKTOWN MEADOWS	WELL 1	WASHOE	GROUNDWATER
145	5	FRANKTOWN MEADOWS	WELL 2	WASHOE	GROUNDWATER
146	5	TRI GENERAL IMPROVEMENT DISTRICT	WELL 1	STOREY	GROUNDWATER
147	5	TRI GENERAL IMPROVEMENT DISTRICT	WELL 3	STOREY	GROUNDWATER
148	5	TRI GENERAL IMPROVEMENT DISTRICT	WELL 8	STOREY	GROUNDWATER
149	5	LAMOILLE VALLEY PLAZA	WELL 1	ELKO	GROUNDWATER
150	5	SLOAN ARMY RESERVE CENTER	WELL 1	CLARK	GROUNDWATER
151	5	ISABELLA PEARL MINE	WELL 1	MINERAL	GROUNDWATER
152	5	ISABELLA PEARL MINE	WELL 3	MINERAL	GROUNDWATER
153	5	BEST WESTERN TOPAZ LAKE INN	WELL 1	DOUGLAS	GROUNDWATER
154	5	RUBY DOME HOLDINGS DBA ELKO RV PARK	WELL 1	ELKO	GROUNDWATER
155	5	RUBY DOME HOLDINGS DBA ELKO RV PARK	WELL 2	ELKO	GROUNDWATER
156	5	PILOT TRAVEL CENTER 485	WELL	HUMBOLDT	GROUNDWATER
157	5	TRAVEL CENTERS OF AMERICA NO 181	WELL 3	PERSHING	GROUNDWATER
158	5	EAST PEAK LODGE	WELL	DOUGLAS	GROUNDWATER
159	5	NPS COTTONWOOD COVE	WELL 1	CLARK	GROUNDWATER
160	5	CARLIN HONOR CAMP NDOC	WELL 1	ELKO	GROUNDWATER

161	5	SAGE SCHOOLS	WELL 1 SAGE SCHOOL	ELKO	GROUNDWATER
162	5	SOUTHERN DESERT CORRECTIONAL CTR NDOC	WELL 2	CLARK	GROUNDWATER
163	5	SOUTHERN DESERT CORRECTIONAL CTR NDOC	WELL 3	CLARK	GROUNDWATER
164	5	SOUTHERN DESERT CORRECTIONAL CTR NDOC	WELL 4	CLARK	GROUNDWATER
165	5	SOUTHERN DESERT CORRECTIONAL CTR NDOC	WELL 5	CLARK	GROUNDWATER
166	5	HUMBOLDT CONSERVATION CAMP NDOC	WELL	HUMBOLDT	GROUNDWATER
167	5	NEVADA GOLD MINES CARLIN GOLDSTRIKE FCTY	EW-14	EUREKA	GROUNDWATER

Table 2: Priority Sample Sites – Outfalls that discharge to surface waterbodies

The table below shows wastewater treatment plant and publicly owned treatment works outfall locations that discharge to surface waterbodies. Outfalls shown in this table are located within priority drinking water protection areas and other drinking water protection areas with a sample priority score greater than zero.

Map ID	WPC Permit Number	Facility Name	Outfall Number	Outfall City	WPC Permit Type Description	Receiving Water Name
1	NV0020150	TRUCKEE MEADOWS WATER RECLAMATION FACILITY	01U	RENO	New & Existing Publicly Owned Treatment Works	TRUCKEE RIVER
2	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	4	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER VIA SPRING SEEP
3	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	05A	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
4	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	2	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
5	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	3	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
6	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	SUM	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
7	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	1	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
8	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	00I	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
9	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	00V	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
10	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	0VI	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
11	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	3	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER VIA SPRING SEEP
12	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	2	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER VIA SPRING SEEP
13	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	1	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER VIA SPRING SEEP
14	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	05C	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
15	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	05B	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER

16	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	5B3	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
17	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	5B1	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
18	NV0023591	BRUNSWICK RECLAIMED WATER STORAGE RESERVOIR	5B2	CARSON CITY	Manufacturing, Commercial, Mining and Silvicultural facility that discharges NON-PROCESS Wastewater	CARSON RIVER
19	NV0023647	CITY OF NORTH LAS VEGAS WATER RECLAMATION FACILITY	2	CLARK COUNTY	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
20	<Null>	TROPICANA/UCD GRADE SEPARATION	1	LAS VEGAS	New & Existing Publicly Owned Treatment Works	LAKE MEAD
21	NV0023647	CITY OF NORTH LAS VEGAS WATER RECLAMATION FACILITY	INF	NORTH LAS VEGAS	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
22	NV0023647	CITY OF NORTH LAS VEGAS WATER RECLAMATION FACILITY	2	CLARK COUNTY	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
23	NV0023647	CITY OF NORTH LAS VEGAS WATER RECLAMATION FACILITY	2	CLARK COUNTY	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
24	NS0040033	YERINGTON WASTEWATER TREATMENT FACILITY	2	YERINGTON	Groundwater Discharge	EFFLUENT PIPE TO CINNAMON POND
25	NV0020061	FALLON WASTEWATER TREATMENT PLANT	01D	FALLON	New & Existing Publicly Owned Treatment Works	NEW RIVER DRAIN VIA UNNAMED DITCH
26	NS0094008	GOLD RANCH WASTEWATER TREATMENT FACILITY	5	VERDI	Groundwater Discharge	NDOT STORM CHANNEL
27	NV0021563	LAUGHLIN WATER RESOURCE CENTER (LWRC)	01D	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
28	NV0021563	LAUGHLIN WATER RESOURCE CENTER (LWRC)	01U	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
29	NV0021563	LAUGHLIN WATER RESOURCE CENTER (LWRC)	1	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
30	NS2008507	LEMMON VALLEY WATER RECLAMATION FACILITY	3	RENO	Groundwater Discharge	SWAN LAKE/WATERS OF THE STATE
31	NS2008500	RENO STEAD WATER RECLAMATION FACILITY	R01	RENO	Groundwater Discharge	SWAN LAKE/WATERS OF THE STATE
32	<Null>	SILVERLAND DEVELOPMENT	1	WASHOE COUNTY	New & Existing Publicly Owned Treatment Works	WASHOE LAKE
33	NV0021563	LAUGHLIN WATER RESOURCE CENTER (LWRC)	01D	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
34	NV0021563	LAUGHLIN WATER RESOURCE CENTER (LWRC)	01U	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
35	NV0021563	LAUGHLIN WATER RESOURCE CENTER (LWRC)	1	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
36	NV0021563	LAUGHLIN WATER RECLAMATION FACILITY	1	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
37	NV0021563	LAUGHLIN WATER RECLAMATION FACILITY	01D	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
38	NV0021563	LAUGHLIN WATER RECLAMATION FACILITY	01U	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
39	NV0021563	LAUGHLIN WATER RECLAMATION FACILITY	1	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
40	NV0021563	LAUGHLIN WATER RECLAMATION FACILITY	01U	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
41	NV0021563	LAUGHLIN WATER RECLAMATION FACILITY	01D	LAUGHLIN	New & Existing Publicly Owned Treatment Works	COLORADO RIVER
42	NS2019504	BATTLE MOUNTAIN WASTEWATER TREATMENT FACILITY	WLP	BATTLE MOUNTAIN	Groundwater Discharge	WETLANDS PONDS

43	NV0020133	CITY OF LAS VEGAS WATER POLLUTION CONTROL FACILITY	2	LAS VEGAS	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
44	NS2008500	RENO STEAD WATER RECLAMATION FACILITY	R12	<Null>	Groundwater Discharge	LONG VALLEY CREEK CA, CA NPDES NEEDED
45	NS2008500	RENO STEAD WATER RECLAMATION FACILITY	R12	<Null>	Groundwater Discharge	LONG VALLEY CREEK CA, CA NPDES PERMIT REQUIRED
46	NV0020133	CITY OF LAS VEGAS WATER POLLUTION CONTROL FACILITY	2	LAS VEGAS	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
47	NV0020061	FALLON WASTEWATER TREATMENT PLANT	1	FALLON	New & Existing Publicly Owned Treatment Works	NEW RIVER DRAIN VIA UNNAMED DITCH
48	NV0020061	FALLON WASTEWATER TREATMENT PLANT	01U	FALLON	New & Existing Publicly Owned Treatment Works	NEW RIVER DRAIN VIA UNNAMED DITCH
49	NV0020133	CITY OF LAS VEGAS WATER POLLUTION CONTROL FACILITY	2	LAS VEGAS	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
50	NV0023167	BATTLE MOUNTAIN SEWAGE TREATMENT FACILITY	1	BATTLE MOUNTAIN	New & Existing Publicly Owned Treatment Works	REESE RIVER AND POTENTIALLY THE HUMBOLDT RIVER
51	NV0020133	CITY OF LAS VEGAS	2	LAS VEGAS	New & Existing Publicly Owned Treatment Works	LAS VEGAS WASH
52	<Null>	COURTHOUSE TANKS	1	ELY	New & Existing Publicly Owned Treatment Works	MURRAY CREEK

Table 3: Priority Sample Sites - Surface Waterbodies

The table below shows surface waterbodies with the highest sample priority scores. Each waterbody reach will be sampled at one location: sample locations forthcoming.

Map ID	Sample Priority Score	Water ID	Water Name	Reach Description	Waterbody Type	County	Region
1	**12**	NV13-CL-42_00	Duck Creek	From its origin to Las Vegas Wash	CREEK	CLARK CO	Colorado River Basin
2	**11**	NV06-SC-69_00	Dry Creek	From its origin to its confluence with Boynton Slough	CREEK	WASHOE CO	Truckee River Basin
3	**11**	NV13-CL-03_00	*Lake Mead	Lake Mead (Nevada portion) excluding area covered by NAC 445A.2154	FRESHWATER RESERVOIR	CLARK CO	Colorado River Basin
4	**11**	NV06-TB-08_00	Lake Tahoe	The entire Lake (Nevada Portion only)	FRESHWATER LAKE	WASHOE CO	Truckee River Basin
5	**11**	NV13-CL-45_00	*Las Vegas Wash above Treatment Plants	Above Treatment Plants	CREEK	CLARK CO	Colorado River Basin
6	**11**	NV13-CL-49_00	Pittman Wash	From its origin to Duck Creek	CREEK	CLARK CO	Colorado River Basin
7	**11**	NV06-SC-42-D_00	Steamboat Creek	From gaging station number 10349300, located in the S 1/2 of section 33, T. 18 N., R. 20 E., M.D.B. & M., to its confluence with the Truckee River	CREEK	WASHOE CO	Truckee River Basin
8	**11**	NV06-SC-79_00	Virginia Lake	The entire lake	FRESHWATER RESERVOIR	WASHOE CO	Truckee River Basin
9	**9**	NV13-CL-40_00	Sloan Channel	From North Las Vegas Blvd. to Las Vegas Wash	CREEK	CLARK CO	Colorado River Basin
10	**9**	NV06-TR-02_00	*Truckee River	From Nevada-California state line to Idlewild	RIVER	WASHOE CO	Truckee River Basin
11	**9**	NV06-TR-05_00	*Truckee River	From Lockwood to Derby Dam	RIVER	WASHOE CO	Truckee River Basin
12	**8**	NV06-TR-57-D_00	Lagomarsino Creek (Long Valley Creek)	Its entire length	CREEK	STOREY CO	Truckee River Basin

13	**8**	NV13-CL-04_00	*Lake Mead Inner Bay	From the confluence of Las Vegas Wash with Lake Mead to 1.2 miles into Las Vegas Bay	FRESHWATER RESERVOIR	CLARK CO	Colorado River Basin
14	**8**	NV06-TR-65_00	Sparks Marina	The entire reservoir	FRESHWATER RESERVOIR	WASHOE CO	Truckee River Basin
15	**7**	NV06-TR-76_00	Alum Creek	From its origin to the Truckee River	CREEK	WASHOE CO	Truckee River Basin
16	**7**	NV06-TR-77_00	Chalk Creek	From its origin to the Truckee River	CREEK	WASHOE CO	Truckee River Basin
17	**7**	NV13-CL-39_00	Flamingo Wash	From its origin to Las Vegas Wash	CREEK	CLARK CO	Colorado River Basin
18	**7**	NV04-HR-02_00	Humboldt River	From Osino to Palisade	RIVER	EUREKA CO	Humboldt River Basin
19	**7**	NV06-TR-39-B_00	Hunter Creek	From Hunter Lake to its confluence with the Truckee River	CREEK	WASHOE CO	Truckee River Basin
20	**7**	NV06-TB-16_00	Incline Creek, East and West Forks, and Incline Creek	The East Fork of Incline Creek from the ski resort to the West Fork of Incline Creek, the West Fork of Incline Creek from State Highway 431 to the East Fork of Incline Creek, and Incline Creek from the confluence of the East and West Forks of Incline C	CREEK	WASHOE CO	Truckee River Basin
21	**7**	NV13-CL-43_00	Tropicana Wash	From its origin to Flamingo Wash	CREEK	CLARK CO	Colorado River Basin
22	**6**	NV06-SC-83_00	Alexander Lake	The entire lake	FRESHWATER RESERVOIR	WASHOE CO	Truckee River Basin
23	**6**	NV08-CR-48_00	All stream/rivers below Lahontan Dam in Lahontan Valley	All stream/rivers below Lahontan Dam in Lahontan Valley except the Lower Carson River, V-Line Canal, and Diagonal Drain	STREAM	CHURCHILL CO	Carson River Basin
24	**6**	NV14-DV-01_00	Amargosa River	Its entire length	RIVER INTERMITTENT	NYE CO	Death Valley Basin
25	**6**	NV04-HR-189_00	California Creek	From its origin to the Foreman Creek	CREEK	ELKO CO	Humboldt River Basin
26	**6**	NV08-CR-10_00	*Carson River	From New Empire to Dayton Bridge	RIVER	LYON CO	Carson River Basin
27	**6**	NV08-CR-13-C_02	*Carson River, Lower	From Carson River Dam to Carson Sink (the natural channel)	RIVER	CHURCHILL CO	Carson River Basin
28	**6**	NV13-CL-02_00	Colorado River	From Hoover Dam to Lake Mojave inlet	RIVER	CLARK CO	Colorado River Basin
29	**6**	NV08-CR-24-C_00	Diagonal Drain	Its entire length	CANAL	CHURCHILL CO	Carson River Basin
30	**6**	NV06-SC-62_00	Evans Creek	From its intersection with Highway 395 to Dry Creek	CREEK	WASHOE CO	Truckee River Basin
31	**6**	NV04-HR-183_00	Fire Creek	Its entire length	CREEK	LANDER CO	Humboldt River Basin
32	**6**	NV04-NF-134_00	Foreman Creek	From its origin to the Humboldt River, North Fork	CREEK	ELKO CO	Humboldt River Basin
33	**6**	NV04-HR-05_00	Humboldt River	From Comus to Imlay	RIVER	PERSHING CO	Humboldt River Basin
34	**6**	NV06-TB-15_00	Incline Creek, East Fork	From its origin to Ski Resort	CREEK	WASHOE CO	Truckee River Basin
35	**6**	NV10-CE-13-B_00	Kingston Creek	Below Groves Lake	CREEK	LANDER CO	Central Region
36	**6**	NV08-CR-46_00	Lahontan Reservoir	The entire reservoir	FRESHWATER RESERVOIR	CHURCHILL CO	Carson River Basin
37	**6**	NV08-CR-33_00	Martin Slough	Its entire length.	CREEK	DOUGLAS CO	Carson River Basin
38	**6**	NV13-CL-31_00	Meadow Valley Wash	From Echo Canyon Reservoir to Caliente	CREEK, INTERMITTENT	LINCOLN CO	Colorado River Basin
39	**6**	NV06-TB-17_00	Mill Creek	From its origin to Lake Tahoe	CREEK	WASHOE CO	Truckee River Basin
40	**6**	NV13-CL-12_02	Muddy River	From Wells Siding Diversion to river mouth at Lake Mead	RIVER	CLARK CO	Colorado River Basin
41	**6**	NV10-CE-32-D_01	*Murry Creek	From its confluence with Gleason Creek to Crawford Street	CREEK	WHITE PINE CO	Central Region
42	**6**	NV04-HR-165_00	North Antelope Creek	From its origin to Antelope Creek	CREEK	ELKO CO	Humboldt River Basin
43	**6**	NV13-CL-33_01	Pahranagat Wash	From Hiko to Lower Pahranagat Reservoir	EPHEMERAL STREAM	LINCOLN CO	Colorado River Basin
44	**6**	NV13-CL-33_02	Pahranagat Wash	From Lower Pahranagat Reservoir to its confluence with the Muddy River	EPHEMERAL STREAM	CLARK CO	Colorado River Basin

45	**6**	NV04-HR-153_00	Rodeo Creek	From its origin to its confluence with boulder Creek	CREEK, INTERMITTENT	EUREKA CO	Humboldt River Basin
46	**6**	NV06-TB-12_00	Third Creek, East and West Forks and Third Creek	The East Fork of Third Creek from State Highway 431 to the West Fork of Third Creek, the West Fork of Third Creek from its origin to the East Fork of Third Creek, and Third Creek from the confluence of the East and West Forks of Third Creek to Lake Tahoe.	CREEK	WASHOE CO	Truckee River Basin
47	**6**	NV04-HR-184_00	Trout Creek	Its entire length	CREEK	HUMBOLDT CO	Humboldt River Basin
48	**6**	NV06-TB-103_00	Unnamed Creek #60 near Fairview Blvd	From its origin to Incline Creek, West Fork	CREEK	WASHOE CO	Truckee River Basin
49	**6**	NV06-TB-106_00	Unnamed Creek near Diamond Peak	From its origin to Incline Creek, East Fork	CREEK	WASHOE CO	Truckee River Basin
50	**6**	NV06-TB-105_00	Unnamed Tributary to Incline Creek @ Tyrolian Village	From its origin to Incline Creek, East Fork	CREEK	WASHOE CO	Truckee River Basin
51	**6**	NV09-WR-09_00	Walker River	From the confluence of Walker River, West and East Forks to the boundary of the Walker River Indian Reservation	RIVER	LYON CO	Walker River Basin
52	**6**	NV09-WR-04_00	Walker River, West Fork	From Wellington to its confluence with the Walker River, East Fork	RIVER	LYON CO	Walker River Basin
53	**6**	NV06-TB-11_00	Wood Creek	From its origin to Lake Tahoe	CREEK	WASHOE CO	Truckee River Basin
54	**5**	NV04-HR-155_00	Brush Creek	From its origin to confluence with Rodeo Creek	CREEK	EUREKA CO	Humboldt River Basin
55	**5**	NV09-WR-18-A_00	Corey Creek	From its origin to the point of diversion of the town of Hawthorne near the West line of section 3, T. 7 N., R. 29 E., M. D. B. & M.	CREEK	MINERAL CO	Walker River Basin
56	**5**	NV09-WR-12_00	Desert Creek	From the Nevada-California state line to the Walker River, West Fork	CREEK	LYON CO	Walker River Basin
57	**5**	NV10-CE-30-C_00	Gleason Creek	From its origin to State Highway 485 (old State Highway 44)	CREEK	WHITE PINE CO	Central Region
58	**5**	NV04-HR-03_00	Humboldt River	From Palisade to Battle Mountain	RIVER	LANDER CO	Humboldt River Basin
59	**5**	NV04-HR-59-C_00	Maggie Creek	From its confluence with Soap Creek to its confluence with the Humboldt River	CREEK	ELKO CO	Humboldt River Basin
60	**5**	NV04-HR-185_00	Rabbit Creek	Its entire length	CREEK	HUMBOLDT CO	Humboldt River Basin
61	**5**	NV08-CR-22-C_00	Rattlesnake (S-Line) Reservoir	Also known as S-Line Reservoir - The entire reservoir	FRESHWATER RESERVOIR	CHURCHILL CO	Carson River Basin
62	**5**	NV04-RR-38-B_00	*Reese River	From its confluence with Indian Creek to State Route 722 (old U.S. Highway 50)	RIVER	LANDER CO	Humboldt River Basin
63	**5**	NV10-CE-22-A_00	Roberts Creek	From its origin to Roberts Creek Reservoir	CREEK	EUREKA CO	Central Region
64	**5**	NV03-SR-03_00	Shoshone Creek	From the Nevada-Idaho state line to its confluence with Salmon Falls Creek	CREEK	ELKO CO	Snake River Basin
65	**5**	NV04-NF-135_00	Stump Creek	From its origin to Foreman Creek	CREEK, INTERMITTENT	ELKO CO	Humboldt River Basin
66	**5**	NV13-CL-07_00	Virgin River	From the Nevada-Arizona state line to Mesquite	RIVER	CLARK CO	Colorado River Basin
67	**5**	NV09-WR-11_00	Walker Lake	The entire lake	FRESHWATER LAKE	MINERAL CO	Walker River Basin

**A different reach of this waterbody will be sampled at an outfall listed in Table 2.*

Per- and Polyfluoroalkyl Substances (PFAS) Nevada Division of Environmental Protection (NDEP) Sampling Project
Sampling Locations

Map ID	WATER_ID	WATER_NAME	Reach Description	Monitoring Station Code	Station Name	Latitude (NAD83)	Longitude (NAD83)	Monitoring Organization	Notes
1	NV13-CL-42_00	Duck Creek	From its origin to Las Vegas Wash	DC_0 - SNWA	Duck Creek near the confluence with Las Vegas Wash	36.0903	-115.0025	SNWA	There are additional monitoring stations in this reach
2	NV06-SC-69_00	Dry Creek	From its origin to its confluence with Boynton Slough	SB22	Dry Creek @ Sierra Pacific	39.4686203	-119.7751007	NDEP	There are additional monitoring stations in this reach
3	NV13-CL-03_00	Lake Mead	Lake Mead (Nevada portion) excluding area covered by NAC 445A.2154	Multiple					Many established monitoring stations exist on Lake Mead
4	NV06-TB-08_00	Lake Tahoe	The entire Lake (Nevada Portion only)	Multiple					Many established monitoring stations exist on Lake Tahoe
5	NV13-CL-45_00	Las Vegas Wash above Treatment Plants	Above Treatment Plants	LW10.75	Las Vegas Wash above City of Las Vegas WWTP Discharge Channel	36.131	-115.0349	BOR, CLV, COH, andSNWA	There are additional monitoring stations in this reach
6	NV13-CL-49_00	Pittman Wash	From its origin to Duck Creek	PW_0 - SNWA	Pittman Wash @ Confluence of Duck Creek	36.08657	-115.0329	SNWA	There are additional monitoring stations in this reach
7	NV06-SC-42-D_00	Steamboat Creek	From gaging station number 10349300, located in the S 1/2 of section 33, T. 18 N., R. 20 E., M.D.B. & M., to its confluence with the Truckee River	SB19	Steamboat Creek @ Cleanwater Way	39.5185089	-119.7042999	NDEP	Steamboat Creek below S.T.P. (T13) = 39.5200615, -119.7036972
8	NV06-SC-79_00	Virginia Lake	The entire lake	VL	Virginia Lake	39.5007	-119.8065	NDEP	
9	NV13-CL-40_00	Sloan Channel	From North Las Vegas Blvd. to Las Vegas Wash	SC_0 - SNWA	Sloan Channel above Confluence with Las Vegas Wash	36.13988	-115.0425	SNWA	There are additional monitoring stations in this reach
10	NV06-TR-02_00	Truckee River	From Nevada-California state line to Idlewild	T2	Truckee River @ Idlewild Park	39.52025	-119.82673	NDEP	There are additional monitoring stations in this reach
11	NV06-TR-05_00	Truckee River	From Lockwood to Derby Dam	T14	Truckee River @ Derby Dam	39.58595	-119.44826	NDEP	There are additional monitoring stations in this reach
12	NV06-TR-57-D_00	Lagomarsino Creek (Long Valley Creek)	Its entire length	LAGO3	Lagomarsino Creek @ Ave de la Couleurs Drive	39.511631	-119.6446991	NDEP	There are additional monitoring stations in this reach
13	NV13-CL-04_00	Lake Mead Inner Bay	From the confluence of Las Vegas Wash with Lake Mead to 1.2 miles into Las Vegas Bay	N/A					The established monitoring stations on Lake Mead Inner Bay are no longer applicable because the water level has dropped in Lake Mead.
14	NV06-TR-65_00	Sparks Marina	The entire reservoir	SMe, SMh, and SMm	Sparks Marina - Epilimnion, Sparks Marina - Hypolimnion, and Sparks Marina - Metalimnion	39.5326691	-119.728302	NDEP	Sparks Marina has other established monitoring stations
15	NV06-TR-76_00	Alum Creek	From its origin to the Truckee River	SB26	Alum Creek @ Truckee River	39.5110283	-119.8554001	NDEP	There are additional monitoring stations in this reach
16	NV06-TR-77_00	Chalk Creek	From its origin to the Truckee River	CHALK	Chalk Creek	39.5100194	-119.8704861	NDEP	There are additional monitoring stations in this reach
17	NV13-CL-39_00	Flamingo Wash	From its origin to Las Vegas Wash	FW_0 - SNWA	Flamingo Wash at Desert Rose GC at outflow from culvert above confluence with LV Wash	36.14017	-115.0506	SNWA	There are additional monitoring stations in this reach
18	NV04-HR-02_00	Humboldt River	From Osino to Palisade	HS6	Humboldt River @ Palisade	40.6092186	-116.2001038	NDEP	There are additional monitoring stations in this reach
19	NV06-TR-39-B_00	Hunter Creek	From Hunter Lake to its confluence with the Truckee River	SB27	Hunter Creek @ Gage	39.4915199	-119.8989029	NDEP	There are additional monitoring stations in this reach
20	NV06-TB-16_00	Incline Creek, East and West Forks, and Incline Creek	The East Fork of Incline Creek from the ski resort to the West Fork of Incline Creek, the West Fork of Incline Creek from State Highway 431 to the East Fork of Incline Creek, and Incline Creek from the confluence of the East and West Forks of Incline C	INCL	Incline Creek @ Lakeshore Drive	39.23987	-119.9448	NDEP	There are additional monitoring stations in this reach
21	NV13-CL-43_00	Tropicana Wash	From its origin to Flamingo Wash	N/A					No established monitoring stations on Tropicana Wash
22	NV06-SC-83_00	Alexander Lake	The entire lake	N/A					No established monitoring stations on Alexander Lake
23	NV08-CR-48_00	All stream/rivers below Lahontan Dam in Lahontan Valley	All stream/rivers below Lahontan Dam in Lahontan Valley except the Lower Carson River, V-Line Canal, and Diagonal Drain	SBCRSR	South Branch Carson River @ Scheckler Road	39.4600601	-118.8370972	NDEP	This monitoring station may not be representative of water quality conditions in all stream/rivers below Lahontan Dam in Lahontan Valley
24	NV14-DV-01_00	Amargosa River	Its entire length	AMG	Amargosa River North of Beatty	36.9191093	-116.7503967	NDEP	
25	NV04-HR-189_00	California Creek	From its origin to the Foreman Creek	CAL	California Creek @ Haul Road	41.4124985	-115.9101028	NDEP	
26	NV08-CR-10_00	Carson River	From New Empire to Dayton Bridge	C11	Carson River @ Dayton Bridge	39.2361603	-119.5879974	NDEP	There are additional monitoring stations in this reach
27	NV08-CR-13-C_02	Carson River, Lower	From Carson River Dam to Carson Sink (the natural channel)	C26	Lower Carson River @ Sheckler Road	39.4830589	-118.8756027	NDEP	Lower Carson River @ Tarzyn Road (C27) = 39.5582809, -118.726799
28	NV13-CL-02_00	Colorado River	From Hoover Dam to Lake Mojave inlet	CL2	Colorado River @ Willow Beach Pier	35.8694496	-114.6619034	NDEP	There are additional monitoring stations in this reach
29	NV08-CR-24-C_00	Diagonal Drain	Its entire length	C30	Diagonal Drain @ Hwy 50	39.4130898	-118.6559982	NDEP	There are additional monitoring stations in this reach
30	NV06-SC-62_00	Evans Creek	From its intersection with Highway 395 to Dry Creek	SB24	Evans Creek @ Sierra Pacific	39.4693909	-119.7779007	NDEP	
31	NV04-HR-183_00	Fire Creek	Its entire length	SW-2-KGSM	Fire Creek Downstream of Fire Creek Mine	40.45625	-116.6364	KLONDEX	There are additional monitoring stations in this reach
32	NV04-NF-134_00	Foreman Creek	From its origin to the Humboldt River, North Fork	FORMAN-1	Foreman Creek Downgradient of Mill Site	41.3964386	-115.8529968	NDEP	There are additional monitoring stations in this reach
33	NV04-HR-05_00	Humboldt River	From Comus to Imlay	HS9	Humboldt River @ Imlay	40.6922493	-118.2185974	NDEP	There are additional monitoring stations in this reach
34	NV06-TB-15_00	Incline Creek, East Fork	From its origin to Ski Resort	EFINCA	Incline Creek Below Diamond Peak	39.24968	-119.9296	NDEP	There are additional monitoring stations in this reach
35	NV10-CE-13-B_00	Kingston Creek	Below Groves Lake	CEN04Kingston-2	Kingston Canyon Creek (Lower)	39.2413597	-117.0278015	NDEP	There are additional monitoring stations in this reach
36	NV08-CR-46_00	Lahontan Reservoir	The entire reservoir	L1	Lahontan Reservoir @ Dam	39.4623985	-119.0675964	NDEP	There are additional monitoring stations in this reach
37	NV08-CR-33_00	Martin Slough	Its entire length.	MARS	Martin Slough Above Confluence East Fork Carson	38.9701805	-119.7978973	NDEP	There are additional monitoring stations in this reach
38	NV13-CL-31_00	Meadow Valley Wash	From Echo Canyon Reservoir to Caliente	N/A					No established monitoring stations on Meadow Valley Wash
39	NV06-TB-17_00	Mill Creek	From its origin to Lake Tahoe	MB	Mill Creek @ Lakeshore Drive	39.2350502	119.9335022	NDEP	There are additional monitoring stations in this reach
40	NV13-CL-12_02	Muddy River	From Wells Siding Diversion to river mouth at Lake Mead	CL11	Muddy River @ Overton	36.5555496	-114.4424973	NDEP	There are additional monitoring stations in this reach
41	NV10-CE-32-D_01	Murry Creek	From its confluence with Gleason Creek to Crawford Street	MURR-1	Murry Creek near Treatment Plant	39.2668686	-114.8703995	NDEP	
42	NV04-HR-165_00	North Antelope Creek	From its origin to Antelope Creek	LAC3	North Antelope Creek @ Fish Pond	41.0900002	-116.5677032	NDEP	There are additional monitoring stations in this reach
43	NV13-CL-33_01	Pahranagat Wash	From Hiko to Lower Pahranagat Reservoir	N/A					No established monitoring stations on Pahranagat Wash
44	NV13-CL-33_02	Pahranagat Wash	From Lower Pahranagat Reservoir to its confluence with the Muddy River	N/A					No established monitoring stations on Pahranagat Wash
45	NV04-HR-153_00	Rodeo Creek	From its origin to its confluence with boulder Creek	N/A					No established monitoring stations on Rodeo Creek
46	NV06-TB-12_00	Third Creek, East and West Forks and Third Creek	The East Fork of Third Creek from State Highway 431 to the West Fork of Third Creek, the West Fork of Third Creek from its origin to the East Fork of Third Creek, and Third Creek from the confluence of the East and West Forks of Third Creek to Lake Tahoe.	N/A					No established monitoring stations on Pahranagat Wash
47	NV04-HR-184_00	Trout Creek	Its entire length	TC1-MMC	Trout Creek Downstream of Marigold Mine Property	40.76262	-117.1501	MARIGOLD	There are additional monitoring stations in this reach
48	NV06-TB-103_00	Unnamed Creek #60 near Fairview Blvd	From its origin to Incline Creek, West Fork	p-TAHCAT08722-060	Unnamed Creek #060 near Fairview Blvd &[BIOP-0081]	39.2638397	-119.9381027	NDEP	
49	NV06-TB-106_00	Unnamed Creek near Diamond Peak	From its origin to Incline Creek, East Fork	U1	Unnamed Creek near Diamond Peak	39.25443	-119.9199	IVGID	
50	NV06-TB-105_00	Unnamed Tributary to Incline Creek @ Tyrolian Village	From its origin to Incline Creek, East Fork	TAH7	Unnamed Tributary to Incline Creek @ Tyrolian Village	39.26001	-119.9243	NDEP	There are additional monitoring stations in this reach
51	NV09-WR-09_00	Walker River	From the confluence of Walker River, West and East Forks to the boundary of the Walker River Indian Reservation	W4	Walker River @ Wabuska	39.1517601	-119.1001968	NDEP	There are additional monitoring stations in this reach

Per- and Polyfluoroalkyl Substances (PFAS) Nevada Division of Environmental Protection (NDEP) Sampling Project
Appendix F: Sampling Locations

52	NV09-WR-04_00	Walker River, West Fork	From Wellington to its confluence with the Walker River, East Fork	W2	West Fork Walker River @ Nordyke West	38.8892899	-119.1793976	NDEP	There are additional monitoring stations in this reach
53	NV06-TB-11_00	Wood Creek	From its origin to Lake Tahoe	WO	Wood Creek @ Lakeshore Drive	39.2435493	-119.9580994	NDEP	There are additional monitoring stations in this reach
54	NV04-HR-155_00	Brush Creek	From its origin to confluence with Rodeo Creek	N/A					No established monitoring stations on Brush Creek
55	NV09-WR-18-A_00	Corey Creek	From its origin to the point of diversion of the town of Hawthorne near the West line of section 3, T. 7 N., R. 29 E., M. D. B. & M.	COR-1	Corey Creek @ Gate	38.4827805	-118.6785965	NDEP	
56	NV09-WR-12_00	Desert Creek	From the Nevada-California state line to the Walker River, West Fork	DC	Desert Creek	38.70173	-119.31976	NDEP	There are additional monitoring stations in this reach
57	NV10-CE-30-C_00	Gleason Creek	From its origin to State Highway 485 (old State Highway 44)	GLEA-1	Gleason Creek at Keystone Junction	39.282819	-114.964375	NDEP	
58	NV04-HR-03_00	Humboldt River	From Palisade to Battle Mountain	HS7	Humboldt River @ Battle Mountain	40.6678200, -116.9311981		NDEP	There are additional monitoring stations in this reach
59	NV04-HR-59-C_00	Maggie Creek	From its confluence with Soap Creek to its confluence with the Humboldt River	HS14	Maggie Creek @ SR 221	40.7198296, -116.0942993		NDEP	There are additional monitoring stations in this reach
60	NV04-HR-185_00	Rabbit Creek	Its entire length	RCM-02	Rabbit Creek Downstream of Confluence of Mine Surface Drainage	41.1912300, -117.1627000		BARRICK	There are additional monitoring stations in this reach
61	NV08-CR-22-C_00	Rattlesnake (S-Line) Reservoir	Also known as S-Line Reservoir - The entire reservoir	C31	S-Line Reservoir @ Outfall	39.4836388, -118.7171021		NDEP	C31 may not be representative of water quality conditions in the reservoir
62	NV04-RR-38-B_00	Reese River	From its confluence with Indian Creek to State Route 722 (old U.S. Highway 50)	HS59	Reese River near Reese River Butte	39.1991692, -117.3445969		NDEP	There are additional monitoring stations in this reach
63	NV10-CE-22-A_00	Roberts Creek	From its origin to Roberts Creek Reservoir	10245970	Roberts Creek nr Eureka, NV	39.7897800, -116.3009000		USGS	
64	NV03-SR-03_00	Shoshone Creek	From the Nevada-Idaho state line to its confluence with Salmon Falls Creek	E9	Shoshone Creek	41.9589195, -114.6526031		NDEP	There are additional monitoring stations in this reach
65	NV04-NF-135_00	Stump Creek	From its origin to Foreman Creek	STC	Stump Creek	41.3802500, -115.9207000		QUEENSTAKE	
66	NV13-CL-07_00	Virgin River	From the Nevada-Arizona state line to Mesquite	CL6	Virgin River @ Mesquite	36.7908592, -114.0935974		NDEP	There are additional monitoring stations in this reach
67	NV09-WR-11_00	Walker Lake	The entire lake	WL3e, WL3h, and WL3m	Walker Lake 3 Center - Epilimnion, Walker Lake 3 Center - Hypolimnion, and Walker Lake 3 Center - Metalimnion	38.7000008, -118.7218018		NDEP	Walker Lake has other established monitoring stations

Appendix D

Sampling Form

Sample Collection Form

Sample Type: Drinking Water / Wastewater / Surface Water (Circle one)

Project: NDEP PFAS Sampling
Client: NDEP
Project #: 23-02-119

Date: _____

Sample ID	Sample Time	Temperature	Conductivity	pH	Turbidity	
	24hr : min	°C	mS/cm	SU	NTU	

Sample Collected: **YES** / **NO** (circle one)

Drinking Water Sample	Outfall Sample	Surface Water Sample	
Facility Name	Outfall Number	Monitoring Station Code	

Sample Location
(Decimal degrees NAD 83)

Latitude	
Longitude	
GPS Accuracy (ft)	

Comments:

Sampler:

Analyses Requested (select all that apply):		Number of Sample Containers	Quality Control Samples (List Duplicate or MS/MSD)
	Method 537.1		
	Method 533		
	Method 1633		

Version 09/13/2023

Appendix E

Chain of Custody Record

Eurofins Eaton Analyitcal: Pomona
941 Corporate Center Drive
Pomona, CA 91678
Phone (626) 386-1100

Chain of Custody Record

eurofins | Environment Testing America

Client Information	Sampler:	Lab PM:	Carrier Tracking No(s):	COC No:
Client Contact:	Phone:	E-Mail:	State of Origin:	Page: Page 1 of
Company:	PWSID:	**Analysis Requested**		Job #:
Address:	**Due Date Requested:**			
City:	**TAT Requested (days):** Standard			
State, Zip:	**Compliance Project:** Δ Yes Δ No			
Phone:	PO #:			
Email:	WO #:			
Project Name:	Project #:			
Site:	SSOW#:			

Preservation Codes:
A - HCL
B - NaOH
C - Zn Acetate
D - Nitric Acid
E - NaHSO4
F - MeOH
G - Amchlor
H - Ascorbic Acid
I - Ice
J - DI Water
K - EDTA
L - EDA
M - Hexane
N - None
O - AsNaO2
P - Na2O4S
Q - Na2SO3
R - Na2S2O3
S - H2SO4
T - TSP Dodecahydrate
U - Acetone
V - MCAA
W - pH 4-5
Y - Trizma
Z - other (specify)
Other:

Sample Identification	**Sample Date**	**Sample Time**	**Sample Type (C=Comp, G=grab)**	**Matrix (W=water, S=solid, O=waste/oil, BT=Tissue, A=Air)**	Field Filtered Sample (Yes or No)	Perform MS/MSD (Yes or No)													Total Number of containers	**Special Instructions/Note:**
			Preservation Code:																	

Possible Hazard Identification
☐ *Non-Hazard* ☐ *Flammable* ☐ *Skin Irritant* ☐ *Poison B* ☐ *Unknown* ☐ *Radiological*

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)
☐ *Return To Client* ☐ *Disposal By Lab* ☐ *Archive For _____ Months*

Deliverable Requested: I, II, III, IV, Other (specify)

Special Instructions/QC Requirements:

Empty Kit Relinquished by:	Date:	Time:	Method of Shipment:

Relinquished by:	Date/Time:	Company	Received by:	Date/Time:	Company
Relinquished by:	Date/Time:	Company	Received by:	Date/Time:	Company
Relinquished by:	Date/Time:	Company	Received by:	Date/Time:	Company

Custody Seals Intact: Δ Yes Δ No	Custody Seal No.:	Cooler Temperature(s) °C and Other Remarks:

Eurofins TestAmerica, Sacramento
880 Riverside Parkway
West Sacramento, CA 95605-1500
phone 916.373.5600 fax 303.467.7248

Chain of Custody Record
Sample Origin: State of Nevada

eurofins | Environment Testing America

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

TestAmerica Laboratories, Inc. d/b/a Eurofins TestAmerica

Client Contact	**Project Manager:**		TALS Project #:
Your Company Name here	**Email:**	**Site Contact:** / **Lab Contact:**	**Date:** / **Carrier:**	COC No: _____ of _____ COCs
Address / City/State/Zip	**Tel/Fax:**			[1] Sampler: [1] **Refer to note below.**
(xxx) xxx-xxxx Phone / (xxx) xxx-xxxx FAX	**Analysis Turnaround Time** ☐ CALENDAR DAYS ☐ WORKING DAYS; TAT if different from Below _____ ☐ 2 weeks ☐ 1 week ☐ 2 days ☐ 1 day			**For Lab Use Only:** Walk-in Client: Lab Sampling:
Project Name: / Site: / P O #				Job / SDG No.:

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)															Sample Specific Notes:

[1] I attest to the validity and authenticity of this (these) sample(s). I am aware that tampering with or intentionally mislabeling the sample(s) location, date or time of collection may be considered fraud and subject to legal action (NAC445.0636)
Signature:_____Date_____

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☑ Return to Client ☐ Disposal by Lab ☐ Archive for_____ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No | Custody Seal No.: | Cooler Temp. (°C): Obs'd:_____ Corr'd:_____ Therm ID No.:_____

Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:

INSTRUCTIONS

1) Choose the correct Eurofins TestAmerica Facility from the pull down list by clicking on cell A1

2) Fill in the appropriate information for your location and phone number

3) Sampler - Fill in name.

4) Provide information on the Regulatory Program to differentiate between Drinking Water & Compliance samples.

5) Choose a default TAT or enter a different one if appropriate

6) Please indicate whether the TAT is Working or Calendar Days

7) In the veritical columns enter the Method/Analysis being requested

8) Fill out the Sample Information -- each line represents one sample

9) Sample Date/Time is required on all samples

10) In the "# of Containers" field enter the total number of bottles for each sample

11) Check Y or N if the sample was filtered in the field (Filtered Sample).

12) Note 'C' for a Composite sample; or 'G' for a Grab Sample.

13) The Sample name should be the one you wish to see in the final report

14) In the cell where the Sample Information intersects the method information please enter the number of containers submitted for the method. Alternatively simply "x" this field

15) In the last row of the eCOC please choose the code for the right preservative used

16) Note any Possible Hazards.

17) Use the Special Instructions field to add any special instructions to the lab

18) If samples are sent across the country, consider indicating the Time Zone where samples were collected

19) Eurofins TestAmerica Terms and Conditions apply for the analysis performed on the submitted samples unless otherwise agreed upon between Eurofins TestAmerica and Company

Appendix F

Laboratory SOPs

EUROFINS EATON ANALYTICAL, LLC
Standard Operating Procedure

EPA Method 533

Confidential

01) Title

Determination of Selected PFAS in Drinking Water by Anion Exchange SPE and LC/MS/MS Using Isotope Dilution

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Attachment:
533-30814-Monrovia r4..11.7.22.pdf (.pdf)

End of document

Version history

Version	Approval	Revision information	
2	24.FEB.2021		
3	21.JUN.2021		
4	18.JAN.2023		

LCMS-EPA 533 Determination of Selected PFAS in Drinking Water by Anion Exchange SPE and LC/MS/MS Using Isotope Dilution

1) SCOPE & APPLICATION

1.1 This is a Solid Phase Extraction (SPE) liquid chromatography/electrospray ionization/tandem mass spectrometry (LC/ESI/MS/MS) method applicable to the determination of selected per- and polyfluorinated alkyl substances (PFAS) in drinking water, groundwater, surface water, bottled water, and treated drinking water sources.

Table 1. EPA Method 533 List of Analytes

Analyte	Acronym	CAS #	MRL, ng/L
9 Perfluoroalkylcarboxylic Acids			
Perfluorobutanoic acid [a]	PFBA	375-22-4	2
Perfluoropentanoic acid [a]	PFPeA	2706-90-3	2
Perfluorohexanoic acid [a]	PFHxA	307-24-4	2
Perfluoroheptanoic acid [a]	PFHpA	375-85-9	2
Perfluorooctanoic acid [a]	PFOA	335-67-1	2
Perfluorononanoic acid [a]	PFNA	375-95-1	2
Perfluorodecanoic acid [a]	PFDA	335-76-2	2
Perfluoroundecanoic acid [a]	PFUnA	2058-94-8	2
Perfluorododecanoic acid [a]	PFDoA	307-55-1	2
6 Perfluoroalkylsulfonic Acids			
Perfluorobutanesulfonic acid [a]	PFBS	375-73-5	2
Perfluoropentanesulfonic acid [b]	PFPeS	2706-91-4	2
Perfluorohexanesulfonic acid [a]	PFHxS	355-46-4	2
Perfluoroheptanesulfonic acid [b]	PFHpS	375-92-8	2

Perfluorooctanesulfonic acid [a]	PFOS	1763-23-1	2
Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7	2
3 Fluorotelomer Sulfonic Acids			
1H,1H,2H,2H-Perfluorohexane sulfonic acid/4:2 Fluorotelomer sulfonic acid [a]	4:2 FTS	757124-72-4	2
1H,1H,2H,2H-Perfluorooctane sulfonic acid/6:2 Fluorotelomer sulfonic acid [a]	6:2 FTS	27619-97-2	2
1H,1H,2H,2H-Perfluorodecane sulfonic acid/8:2 Fluorotelomer sulfonic acid [a]	8:2 FTS	39108-34-4	2
7 Perfluoroalkyl Ether Carboxylic Acids and Others			
Hexafluoropropylene oxide dimer acid [a]	HFPO-DA/GenX	13252-13-6	2
4,8-Dioxa-3H-perfluorononanoic acid [b]	ADONA	919005-14-4	2
9-Chlorohexadecafluoro-3-oxanone-1-sulfonic acid [b]	9Cl-PF3ONS/ F-53B major	756426-58-1	2
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid [b]	11Cl-PF3OUdS/ F-53B minor	763051-92-9	2
Perfluoro-4-methoxybutanoic acid [b]	PFMBA/PFMOBA	863090-89-5	2
Perfluoro-3-methoxypropanoic acid [b]	PFMPA/PFMOPrA	377-73-1	2
Nonafluoro-3,6-dioxaheptanoic acid [b]	NFDHA/PFMOEOAA	151772-58-6	2

Notes: [a]: 16 PFAS analyzed by using an isotope dilution method. [b]: 9 PFAS analyzed by using an internal standard method.

4:2 FTS also called 4:2 Fluorotelomer sulfonic acid, 6:2 FTS also called 6:2 Fluorotelomer sulfonic acid, 8:2 FTS also called 8:2 Fluorotelomer sulfonic acid, NFDHA also called Perfluoro-2-methoxyethoxyacetic acid (PFMOEOAA), HFPO-DA/GenX (acid form) also called perfluoro-2-propoxypropanoic acid (PFPrOPrA), and ADONA (acid form) also called dodecafluoro-3H-4,8-dioxanonanoic acid.

9Cl-PF3ONS/F-53B major is also available as K salt form (CAS No. 73606-19-6). 11Cl-PF3OUdS/F-53B minor is also available as K salt (CAS No. 83329-89-9). ADONA is available as ammonium salt (CAS No. 958445-44-8) and Na salt (no CAS No.).

1.2 Applicable concentration ranges are 2-80 ng/L.

1.3 Analysts performing this method must have a clear understanding of solid phase extraction (SPE) and LC/ESI/MS/MS principles and also have demonstrated experience in the use of LC/ESI/MS/MS.

2) SUMMARY OF METHOD

2.1 A 250 mL water sample fortified with isotopically labeled analogues of the method analytes is extracted through a weak anion/mixed-mode polymeric solid phase extraction (SPE) cartridge containing weak anion, mixed-mode polymeric sorbent with a styrenedivinylbenzene (SDVB) backbone and a di-amino ligand. The cartridge is rinsed with sequential washes of aqueous ammonium acetate and methanol. Then the analytes and their isotope dilution analogues are eluted from the solid phase sorbent with a small quantity of methanol containing ammonium hydroxide. The extract is then evaporated to dryness with nitrogen and heated water bath at less than 60°C, reconstituted with 20% water in methanol (v/v), spiked with the Isotope Performance Standards (IPS), and then adjusted to 1.0 mL with 20% water in methanol.

2.2 An aliquot of the sample extract is injected onto a C18 column. The analytes, isotope dilution analogues, and internal standards are separated by using a gradient composition of methanol and 20 mM ammonium acetate in reagent water as the mobile phase. After elution from the column, the analytes are detected by ESI/MS/MS in a multiple reaction monitoring (MRM) mode. In the negative ESI process, a deprotonated molecular ion (M-H) is typically formed. In the MS/MS process, these precursor ions then form product ions which are used for quantitation.

2.3 A minimum of five points are used to generate a linear or 6 points for quadratic calibration curves for the analytes using peak area and an isotope dilution technique. The calibration function is forced thru the origin. IPS and IDA/SS are calibrated using Average Response factor as these are added at a single concentration level to the calibration standards. The IDA/SS uses an internal standard technique. The IPS/IS uses an external calibration technique.

2.4 Routine quality assurance is performed by analyzing IPS/IS, IDA/SS, Continuing Calibration Checks (CCC), Laboratory Reagent Blanks (LRB/MBLK), Laboratory Fortified Blanks (LFB/LCS), Laboratory Fortified Sample Matrix (LFSM/MS), Laboratory Fortified Sample Matrix Duplicate (LFSMD/MSD), Field Duplicates (FD/DUP), Field Reagent Blank (FRB)), and external Quality Control Standard samples (QCS).

3) DEFINITIONS

3.1 Refer to the WI26472, Glossary for a complete list of terms and definitions.

3.2 Isotope Dilution Analogues (IDA)/Surrogate Standards (SS) – Isotopically labeled analogues of the method analytes that are added to the sample prior to extraction in a known amount. Note: Not all target PFAS currently have an isotopically labelled analogue. In these cases, an alternate isotopically labelled analogue is used as recommended in the Table 5 of the method.

3.3 Isotope Performance Standards (IPS)/Internal Standards (IS) – Quality control compounds that are added to all standard solutions and extracts in a known amount and used to measure the relative response of the isotopically labelled analogues that are components of the same solution. For this method, the isotope performance standards are three isotopically labeled analogues of the method analytes. The isotope performance standards are indicators of instrument performance and are used to calculate the recovery of the isotope dilution analogues through the extraction procedure. In this method, the isotope performance standards are not used in the calculation of the recovery of the native analytes.

4) INTERFERENCES

4.1 Method interferences may be caused by multiple sources. All sources or items must be routinely demonstrated to be free from the interferences. An LRB can provide information regarding the presence or absence of such interferences and needs to be less than 1/3 the MRL for the method analytes. **Note:** Subtracting blank values from sample results is not permitted.

4.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles, autosampler vials, and other sample processing hardware.

4.2.1 LCMS grade methanol are proven to be satisfactory for this method.

4.2.2 Ammonium acetate used as a preservative potentially contains trace-level organic contaminants including PFAS.

4.2.3 Care should be taken when using gastight syringes for this method because Teflon may cause leaching PFAS contamination to samples and standards.

4.3 The SPE cartridges may be a source of interferences. Variations from lot to lot and from brand to brand may be significant to preclude analyte extraction, identification, and quantitation. Therefore, brands and lots of SPE cartridges must be recorded tested prior to use on samples to ensure that contamination does not preclude analyte identification and quantitation. A method blank (MBLK) and MRL check must be extracted and analyzed to demonstrate the SPE cartridge is free of contamination

4.4 The SPE system such as a vacuum manifold or an AutoTrace unit may be a source of interferences. All items such as these must routinely be demonstrated to be free from interferences. In order to minimize PFAS carryover on the system during extraction, the system is fully flushed with at least 50 mL of methanol before initiating a new extraction batch.

4.5 Method interferences may also be caused by contaminants: 1) in the liquid delivery system (including the solvent and in-line filters, the needle and seal pack, the plunger and seal wash, and the sample loop) and 2) in the ion generation and sampling system (including the ESI probe capillary, the sample cone, the extraction cone, and the ion block). All items such as these must routinely be demonstrated to be free from interferences. In order to minimize PFAS buildup on the system during mobile phase equilibration, the system may be flushed with 100% methanol for at least 10 minutes before initiating a sequence.

4.5.1 Carryover peaks from one analysis will affect the proper detection of analytes in a subsequent analysis. Carryover peaks may result from a sample containing high concentrations of analytes. An adequate amount of rinsing solvents for needle wash and seal pack wash are pumped through the system to clean the seal pack, needle, and sample loop. However, the analyst must carefully review data from samples analyzed immediately after high concentration samples. Also, after analysis of a sample containing high concentrations of analytes, an instrument blank can be run to ensure that accurate values are obtained for next sample.

4.6 Method interferences may also 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. High levels of humic and/or fulvic material that is co-extracted by this method can cause enhancement and/or suppression in the ESI source. For this method, total organic carbon (TOC) is a good indicator of humic content of the sample.

4.7 The method involves the extraction and concentration of trace levels of PFAS. As such, PFAS standards, extracts and samples must not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAS analytes, IPS

and IDA standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers.

4.8 The mass-labeled standards used as IPS and IDA may contain a small percentage of the corresponding native analyte or different mass-labeled analogs. The labeled standards must meet the purity requirements stated in the low system background requirement in Section 14.

4.8.1 A trace amount of $^{13}C_3$-PFBA may be present in $^{13}C_4$-PFBA. Natural abundance (1.1%) of ^{13}C present in $^{13}C_3$-PFBA may empirically contribute to the peak areas of $^{13}C_4$-PFBA.

4.8.2 Natural abundance (4.25%) of ^{34}S present in the corresponding native analyte may empirically contribute to the peak areas of M+2 ions from $^{13}C_2$-labeled telomere sulfonates (4:2 FTS, 6:2 FTS, and 8:2 FTS).

4.9 Inorganic Salts – Acceptable performance defined as recovery of the isotope dilution analogues between 50–200% was confirmed for matrix ion concentrations up to 250 mg/L chloride, 250 mg/L sulfate, and 340 mg/L hardness measured as $CaCO_3$. Higher matrix ion concentrations may result in unacceptable performance.

5) PERSONNEL HEALTH & SAFETY

5.1 Toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Consult the OSHA regulations and the SDS for all analytes, IDA, and IS for proper handling procedures. SDS are available to laboratory personnel at https://msdsmanagement.msdsonline.com/5c1df5b3-747d-4789-8104-42457dc3a3e5/ebinder/?nas=True.

5.2 PFOA has been described as "likely to be carcinogenic to humans." Pure standard materials and stock standard solutions of these method analytes should be handled with suitable protection to skin.

5.3 Wear eye protection and gloves when working with these chemicals.

5.4 Refer to the SOP "Hazardous Waste Management and Sample Disposal Procedures," Chemical Hygiene Plan and OSHA Standard 29 CFR 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories; Final Rule for additional safety information.

6) EQUIPMENT & SUPPLIES

7) REAGENTS & STANDARDS

8) SAMPLE COLLECTION, PRESERVATION & STORAGE

8.1 Sample Collection and Preservation – Nitrile gloves must be used when preserving bottles at the laboratory and also for collecting samples. Samples are collected in three 250 mL pre-preserved with ammonium acetate polypropylene bottles (actual volume = 280 mL to the neck) fitted with polypropylene screw caps. Alternatively, prior to shipping, 0.28 g (0.25-0.3 g) solid ammonium acetate (1 g/L) must be added to each sample container

8.1.1 The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles.

8.1.2 Subsampling from a single bottle is not permitted except exceeding the calibration range as described in Section 12.5.

8.1.3 A Field Reagent Blank (FRB) sample must be handled along with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. A FRB containing the reagent water must be shipped to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (with preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FRB and pour the pre-analyzed reagent water into the empty shipped preserved sample bottle, seal and label this bottle as the FRB. The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAS are not introduced into the sample during sample collection/handling.

8.1.3.1 The same lots of the preservative and sample bottles must be used for the FRBs as for the field samples.

8.1.3.2 Reagent water used for the FRBs must be analyzed prior to shipment to ensure the water has minimal residual PFAS. Extract and analyze an LRB prepared with reagent water

using the same lots of the preservative and sample bottles destined for shipment to the sampling site. Ensure that analyte concentrations are < 1/3 the MRL.

8.2 Sample Shipment and Storage – Valid samples must be chilled on ice in a cooler during shipment, received within 2 days of collection, and below 10 ºC at the laboratory. Samples must be stored at or below 6 ºC and protected from light until extraction. If samples are received more than 2 days after collection, samples must not exceed 6 ºC. Verify sample temperature upon receipt. Check residual chlorine within 3 days upon receipt.

8.3 Sample Holding Time – The maximum holding time for samples to be extracted is 28 days from collection.

8.4 Extract Holding Time – The maximum holding time for sample extracts is 28 days after sample extraction. Store refrigerated at 4±2℃. Bring samples to room temperature prior to analysis.

9) QUALITY CONTROL

9.1 The Quality Control Requirements of this method are presented in table form in Attachment V. Both Extraction Batch and Analysis Batch size are limited to 20 field samples.

9.2 Before analyzing any samples, the laboratory must meet the requirements of the Initial Demonstration of Capability (IDC) found in Section 14.

9.3 Isotope Performance Standards (IPS) – Add the IPS to all the calibration, QC, and field samples prior to analysis. For calibration standards, continuing calibration check, QC and field samples, the IPS response (as indicated by peak area) must be within 50-150% of the average IS area measured during the initial calibration.

9.3.1 If the criteria are not met, all data for the analytes must be considered invalid for all associated samples in the analysis batch. Corrective actions must be taken as described in Section 10.6. The analyst must reanalyze the sample as part of the same or a new analysis batch after the problems have been resolved or report the data with appropriate qualifications.

9.3.2 If the reanalysis meets the IS recovery criterion, report only the reanalysis data.

9.3.3 If the reanalysis does not meet the IPS recovery criteria, reextraction must be performed if the samples are still within the holding time or the data must be qualified. If reextraction is not possible, the ASM must be contacted in order to resolve the issue with the client.

9.4 Isotope Dilution Analogues (IDA) – Add the IDA to all the calibration, QC, and field samples prior to extraction or analysis. Calculate the percent recovery using the equation in Section 13.1. The IDA recovery in QC and field samples must be within 50-200% of the true value. IDA recovery in the calibration standards, CCCs, and QCS must be within 70-130% of the true value

9.4.1 If the IDA criteria are not met, all data for the analytes must be considered invalid for all associated samples in the analysis batch. Corrective actions must be taken as described

in Section 10.6. The analyst must reanalyze the sample as part of the same or a new analysis batch after the problems have been resolved.

9.4.2 If the reanalysis meets the IDA criteria, report only the reanalysis data.

9.4.3 If the reanalysis does not meet the IDA criteria, reextraction must be performed if the samples are still within the holding time. If reextraction is not possible, the ASM must be contacted in order to resolve the issue with the client.

9.5 Unextracted Quality Control Sample (QCS) (ICV, etc in TALS) – At a minimum, a QCS at mid-level calibration concentration must be run as part of the IDC, and at least quarterly. Calculate the percent recovery using the equation in Section 13.1. The QCS percent recovery for each analyte must be within 70-130% of the true value.

9.5.1 If the criteria are not met, then all calibration, QC, and field sample data must be considered invalid. Corrective actions must be taken as described in Section 10.6. The analyst must reanalyze all the calibration, QC, and field samples after the problems have been resolved.

9.6 Continuing Calibration Checks (CCCs)(CCV,CCCL, CCVIS, etc in TALS) – A low-level CCC (CCL) at 0.5 µg/L must be run immediately after initial calibration curve, prior to running the QCS, any QC and field samples. Subsequent CCCs must be run after every ten field samples and at the end of each analysis batch, and is rotated between a mid-level CCC (CCM) at 7.5µg/L and a high-level CCC (CCH) at 15µg/L. If ten or fewer samples are analyzed, the ending CCC is rotated between CCM and CCH with each batch. Calculate the percent recovery using the equation in Section 13.1. CCL recoveries must be within 50-150% of the true value, CCM and CCH recoveries must be within 70-130% of the true value for each analyte. Mathematically, for 0.5µg/L to 20µg/L calibration range, the midpoint concentration is 10µg/L. UCMR 4 defines midpoint as ±20% of mathematical midpoint. In this case, ±20% of 10µg/L is 8µg/L to 12µg/L. For ease in standard preparation, CCM was assigned a concentration of 7.5µg/L

9.6.1 If the CCC criteria are not met, then all data since the last passing CCC must be considered invalid. Corrective actions must be taken as described in Section 10.6. Any field samples analyzed since the last acceptable CCC must be reanalyzed as part of the same or a new analysis batch after the problems have been resolved with the following exception. For a particular target analyte, if the CCC fails because the recoveries are greater than the upper recovery limits, and field samples show no detection, non-detects may be reported without reanalysis. **Note**: there may be further requirements from ASMs for flagged data, however this is not a concern for operations staff.

9.7 Laboratory Reagent Blanks (LRB)(MB, MBL, etc in TALS) – Include at least one LRB with each extraction batch including a set of up to 20 samples. The target analytes must be less than 1/3 the MRL. Any time a new lot of SPE cartridges is received, an LRB must be performed. If a target analyte is detected in the LRB at concentrations greater than or equal to 1/3 the MRL, then all data for the analyte must be considered invalid for all associated samples in the extraction batch. Corrective actions must be taken as described in Section 10.6. The analyst must reanalyze the LRB as part of the same or a new analysis batch after the problems have been resolved. **Note:** Subtracting blank values from sample results is not permitted.

9.7.1 If the reanalysis meets the LRB acceptance criteria, report only the reanalysis data.

9.7.2 If the reanalysis does not meet the LRB criteria, re-extraction of all samples with results above MRL must be performed. If re-extraction is not possible, the ASM must be contacted in order to resolve the issue with the client.

9.8 Laboratory Fortified Blank (LFB/LCS) – Include one low level (2 ng/L) LFB/LCS with each extraction batch including a set of up to 20 samples. Then, mid (30 ng/L) and high (60 ng/L) LFB/LCS levels must be rotated between extraction batches. This is illustrated in the following table:

Batch 1: LFB low/MRL Check and LFB/LCS-Mid
Batch 2: LFB low/MRL Check and LFB/LCS-High
Batch 3: LFB low/MRL Check and LFB/LCS-Mid
Batch 4: LFB/LCS-low and LFB/LCS-High
Batch 5: LFB/LCS-Mid and LFB/LCS-Mid
Batch 6: LFB/LCS-High and LFB/LCS-High
etc.

9.8.1 Calculate the percent recovery using the equation in Section 13.1. The LFB/LCS percent recovery for each analyte must be within 50-150% of the true value for the low level, and 70-130% of the true value for the medium and high levels.

9.8.2 If the criteria are not met for the LFB/LCS, corrective actions must be taken. LFBD/LCS2 if analyzed immediately after the LFB/LCS may serve as the corrective action. Additional corrective actions are described in section 10.6. The analyst must reanalyze the LFB as part of the same or a new analysis batch after the problems have been resolved.

9.8.3 If the reanalysis meets the LFB/LCS criteria, report only the reanalysis data.

9.8.4 If the reanalysis does not meet the LFB criteria and LFBD/LCS2 failed to meet criteria, re-extraction of the entire extraction batch must be performed. If re-extraction is not possible, the ASM must be contacted in order to resolve the issue with the client to resample.

9.8.5 Any time a new lot of SPE cartridges is received, an LRB and low level LFB/MRL Check must be performed. The target analytes must be less than 1/3 the MRL in the LRB. Calculate the percent recovery in the low level LFB/MRL Check using the equation in Section 13.1. The low level LFB/MRL Check percent recovery for each analyte must be within 50-150% of the true value.

9.10 Laboratory Fortified Sample Matrix (LFSM/MS) – Include at least one LFSM/MS with each extraction batch including a set of up to 20 samples. The fortification concentrations must be alternated between a low, mid, and high-level concentration. The low-level (LFSM/MS-Low) fortification concentration must be at or below the MRL for each analyte. The mid-level (LFSM/MS-Mid) fortification concentration must be near the mid-level calibration standard for each analyte. The high-level (LFSM/MS-High) fortification concentration must be near the high-level calibration standard for each analyte. LFSM/MS-Low is at 2 ng/L, LFSM/MS-Mid is at 30 ng/L, and LFSM/MS-High is at 60 ng/L.

9.10.1 Calculate the percent recovery using the equation in Section 13.2. For fortification levels at the MRL, the percent recovery must be within 50-150% of the true value. Recoveries for samples fortified at all other concentrations must be within 70-130% of the true value.

9.10.2 If the results are outside of the designated recovery range, and the recovery for that analyte is shown to be in control in the CCCs and LFB/LCSs, the recovery problem for the LFSM/MS is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect based on poor recoveries in the matrix spike to inform the data user that the results are suspect.

9.11 Laboratory Fortified Sample Matrix Duplicate (LFSMD/MSD) or Field Duplicate (FD/DUP) – Include at least one LFSMD/MSD or FD/DUP with each extraction batch including a set of up to 20 samples. Like LFSM/MS, the fortification concentrations must be alternated between a low, mid, and high-level concentration. Use the same LFSM/MS fortification concentrations and recovery criteria. An extraction batch that contains an LFSMD/MSD does not require a FD/DUP.

9.11.1 Calculate the percent recovery using the equation at Section 13.2 to calculate percent recovery. For analyte concentrations within two times the MRL, the percent recovery must be within 50-150% of the true value. Recoveries for all other concentrations must be within 70-130% of the true value.

9.11.2 If the results are outside of the designated recovery range, and the recovery for that analyte is shown to be in control in the CCCs and LFB/LCSs, the recovery problem for the LFSMD/MSD is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect based on poor recoveries in the matrix spike to inform the data user that the results are suspect.

9.11.3 Calculate the relative percent difference (RPD) for sample duplicate measurements using the equation in Section 13.3. For analyte concentrations within a factor of two times the MRL, the RPDs must be less than or equal to 50%. For analyte concentrations greater than two times the MRL, the RPDs must be less than or equal to 30%. If the RPD falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs and LFB/LCSs, the recovery is judged matrix biased. The results for the sample are labeled as suspect based on poor RPD values to inform the data user that the results are suspect. For Arizona samples, if RPD failed, then run LFB/LFBD (LCS/LCSD) to obtain precision and accuracy

9.12 Field Reagent Blank (FRB) – Analysis of the FRB is required only if an associated Field Sample contains an analyte greater than or equal to the MRL. The FRB target analytes must be less than or equal to 1/3 the MRL. If a target analyte is detected in the FRB at concentrations greater than 1/3 the MRL, verify that the source of the contamination is due to sample collection/handling or carryover of samples containing high concentrations of analytes. Then reanalyze the FRB in a separate analytical batch or in the same analytical batch following an LIB, must either confirm or not confirm the analyte's presence in the FRB. If the reanalysis passes the FRB requirement, all samples collected with the passing FRB are valid. If the reanalysis still fails the FRB requirement, all samples with results greater than MRL collected with the failed FRB are invalid, recollected, and reanalyzed, and the ASM must be contacted in order to resolve the issue with the client.

9.13 Evaluation of Background When Analytes Exceed the Calibration Range – After analysis of a sample in which method analytes exceed the calibration range, one or more LRBs must be analyzed (to detect potential carryover) until the system meets the LRB acceptance criteria. If this occurs during an automated sequence, examine the results of samples analyzed following the sample that exceeded the calibration range. If the analytes that exceeded the calibration range in the previous sample are detected at, or above, the

MRL, these samples are invalid. If the affected analytes do not exceed the MRL, these subsequent samples may be reported.

9.14 Lab Instrument Blank (LIB) Optional – Analysis of the LIB may be done at the beginning of the run and after the highest calibration point to demonstrate that there is no carryover. If analyzed, the target analytes must be less than 1/3 the MRL. If a target analyte is detected in the LIB at concentrations greater than or equal to 1/3 the MRL, Analysis run must be repeated.

9.15 Qualitative/Semi-Quantitative PFOA Mixed Standard – Analyze a technical grade PFOA at a mid to high concentration as a retention time check prior to running initial demonstration of capability (IDC). Repeat anytime chromatographic changes occur that alter analyte retention time. Both the linear and branched isomers must be within the acquisition window. This standard is not used for quantitation, but for identification of the branched and linear isomers for integration of QC and field samples.

9.16 QC exception reports are generated for failing QC, and QC tracking will be performed at that time.

10) PREVENTIVE MAINTENANCE & TROUBLESHOOTING

10.1 Mechanical Pump Ballasting – At least once per week, ballast the mechanical pump by opening (turn counterclockwise to full open) the gas ballast knob on top of the pump. Leave the knob in this position for 15-20 min, then close tightly. This allows oil in the pump filter reservoir to drain back into the pump body. **Note:** DO NOT perform any data acquisitions during this time. Also, do not ballast the pump for longer than 30 minutes.

10.2 Mechanical Pump Oil Check and Change – Periodically check the oil level in the roughing pump when performing ballasting. The oil should be relatively clear and pale yellow in color and in the working range. Change the pump oil as needed using high grade Edwards or Alcatel pump oil.

10.3 Curtain plate Cleaning – It may become necessary to clean the curtain plate (the outer plate which is at atmospheric pressure). The cone needs to be cleaned when sensitivity drops or there appears to be a lot of noise in the baseline.

10.3.1 Gently clean the curtain plate with aluminum oxide grit. Rinse with reagent water then methanol. Dry with nitrogen gas and re-install. **IMPORTANT:** Do not set the conical part side down as this may damage the orifice.

10.4 Purging the Pump – The LC pumps needs to be purged whenever eluents are replaced. Open the purge valve and select "Purge" on the keypad.

10.5 Guard Column Replacement – Replace the guard column as necessary. Particulates resulting from SPE sorbent breakthrough and the mobile phase may easily clog the guard column and the analytical column.

10.6 Corrective Action – Preparation and reanalysis must be performed after problems have been resolved. In order to locate problems, analysts should check:

1) calculations to locate possible errors,
2) contamination,
3) standard solutions for degradation, and

4) instrument performance problems.

Corrective actions may include:

1) reprepare all samples,
2) prepare and use new stock and substock standard solutions,
3) prepare and use a new mobile phase,
4) install a new analytical column,
5) retune the instrument to optimize the performance, and
6) check and perform instrument maintenance.

10.6.1 ESI/MS instrument maintenance may include:

1) clean and repair the ESI probe,
2) clean the ion source and sampling cone,
3) perform mass calibration and retune the instrument,
4) clean hexapole and quadrupole,
5) change pump oil, and
6) other maintenances.

10.6.2 LC instrument maintenance may include:

1) prime seal wash and needle wash,
2) perform compression check and adjust seals,
3) purge the sample management system,
4) replace solvent inlet filters and the in-line filter element,
5) replace needle and seal pack,
6) replace pump check valves,
7) maintenance of LC pump components, and
8) other maintenances.

11) CALIBRATION & STANDARDIZATION

12) PROCEDURE

13) DATA PROCESSING, DATA EVALUATION, & CALCULATIONS

13.1 Calculation of Percent Recovery - Use the following equation to calculate percent recovery:

$$\%R = \left(\frac{A}{B}\right) \times 100$$

where:
A = measured concentration in the fortified sample
B = fortification concentration.

13.2 Calculation of Percent Recovery for Lab Fortified Sample Matrices:

$$\%\,R = \frac{(A-B)}{C} \times 100$$

where:
A = measured concentration in the fortified sample,
B = measured concentration in the unfortified sample at or above the MRL.
C = fortification concentration.

13.3 Calculation of Relative Percent Difference (RPD):

13.3.1 For duplicate analysis of field sample:

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2) \div 2} \times 100$$

13.3.2 For duplicate analysis of lab fortified matrices:

$$RPD = \frac{|LFSM - LFSMD|}{(LFSM + LFSMD) \div 2} \times 100$$

13.4. Because environmental samples may contain both branched and linear isomers for method analytes, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes, integration and quantitation of the PFAS is dependent on type of standard available for each PFAS. It is recognized that some of the procedures described below for integration of standards, QC samples and Field Samples may cause a small amount of unavoidable bias in the quantitation of the method analytes due to the current state of the commercially available standards.

13.4.1 Multiple chromatographic peaks may be observed for standards of PFHxS and PFOS due to chromatographic resolution of the linear and branched isomers of these compounds. All the chromatographic peaks observed in these standards must be integrated and the areas summed. Chromatographic peaks in all Field Samples and QC samples must be integrated in the same way as the calibration standards for analytes with quantitative standards containing the branched and linear isomers.

13.4.2 For PFOA, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and compare retention times and tandem mass spectrometry transitions. Quantitate Field Samples and QC 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 with a linear-isomer quantitative PFOA standard.

13.4.3 If standards containing the branched and linear isomers cannot be purchased (i.e., only linear isomer is available), only the linear isomer can be identified and quantitated in Field Samples and QC samples using the linear standard because the retention time of the branched isomers cannot be confirmed.

13.4 Process the QC and samples using the appropriate quantitation method. Update the retention times of the analytes and make any adjustments to the peak detection parameters if necessary. If changes are made, reprocess the samples before continuing.

13.5 Review data file for any incorrect peak identification and integration. Manual integrations are performed when the retention time or baseline designated by the software is incorrect.

13.6 Save the data and print out reports as noted below. Export the data to the LIMS and report the results through Data Entry.

14) METHOD PERFORMANCE

An acceptable analyte calibration must be demonstrated and documented before performing the IDC.

14.1 Initial Demonstration of Capability (IDC) – All requirements of the IDC must be successfully performed prior to analyzing any Field Samples and for each analyst performing this method.

14.1.1 Initial Demonstration of Branched *vs.* Linear Isomer Profile for PFOA in a Qualitative Standard – Prepare and analyze a mid to high concentration technical grade PFOA and identify retention times of branch isomers of PFOA. This qualitative standard is NOT used for quantitation, but for identification of the branched and linear isomers for integration of QC and field samples. Repeat anytime chromatographic changes occur that alter analyte retention time.

14.1.2 Initial Demonstration of Low System Background – Prepare, extract and analyze an LRB immediately after injecting the highest calibration standard. If an automated SPE system is used, an LRB much be extracted on each port to fulfill this requirement. The LRBs are be rotated among the ports to ensure that all the valves and tubing meet the LRB requirements. The target analytes for the LRB must be less than 1/3 the MRL.

14.1.3 Initial Demonstration of Accuracy – Prepare, extract, and analyze 7 replicate LFBs (containing sample preservatives) fortified at 30 ng/L. The acceptable average recovery is 70-130% for all target analytes.

14.1.4 Initial Demonstration of Precision – Using the same set of replicate data generated for Section 14.1.3, calculate the relative standard deviation (RSD). The RSD must be less than 20% for all target analytes.

14.1.5 Minimum Reporting Limit Confirmation (PIR Study)– This procedure must be completed initially on each instrument performing this method. PIR is required for new instrument and new analyst.

14.1.5.1 Prepare, extract, and analyze 7 replicate LFBs at the estimated MRL. Determine the Half Range for the Prediction Interval of Results (HRPIR) using the equation below:

$$HR_{PIR} = 3.963 * SD$$

where:
SD = the standard deviation, 3.963 is a constant value for seven replicates.

14.1.5.2 Confirm that the upper and lower limits for the Prediction Interval of Results (PIR = Mean ± HR_{PIR}) meet the upper and lower recovery limits as shown below

The Upper PIR Limit must be ≤ 150%.

$$\frac{\text{Mean} + HR_{PIR}}{\text{Fortified Concentration}} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥ 50%.

$$\frac{\text{Mean} - HR_{PIR}}{\text{Fortified Concentration}} \times 100 \geq 50\%$$

14.1.5.3 The MRL is validated if both the Upper and Lower PIR Limits meet the criteria. If these criteria are not met, the MRL has been set too low and must be determined again at a higher concentration.

14.1.6 Method Detection Limit (MDL) – The MDL is not required by this method, however state certification may require MDL study. If annual MDL studies are needed, follow the detailed instructions in Method Detection Limit (MDL) Procedure, Document number W125066. Data should be entered into the MDL Study spread sheet. The method detection limit (MDL) procedure and calculation is based on EPA's procedure "Definition and Procedure for the Determination of the Method Detection Limit, Revision 2".

14.2 Continuing DOC must be performed on an annual basis according to form 06-QA-F0400.

15) POLLUTION PREVENTION

15.1 This method utilizes SPE to extract analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment as compared to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

15.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036.

16) WASTE MANAGEMENT

16.1 It is the responsibility of the laboratory to determine whether its wastes are hazardous and to assure safe handling and disposal. The laboratory works closely with the Treatment, Storage, and Disposal Facility to ensure that certain wastes are recycled where possible, that the source of waste is reduced to the lowest possible level and that stringent land disposal restrictions are followed.

16.2 Refer to the following documents for additional information regarding waste management:

16.2.1 Hazardous Waste Management and Sample Disposal Procedures

16.2.2 Resource Conservation and Recovery Act (RCRA)-Title 40 of the Code of Federal Regulations, Parts 260 through 270 (40 CFR 260-270)

16.2.3 California Hazardous Waste Control Law (HWCL)-CCR Title 22 where 40 CFR was duplicated into CCR Title 22, Parts 66260-66270.

17) REFERENCES

17.1 U.S. Environmental Protection Agency (USEPA) Method 533 Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry, November, 2019, EPA Document No. 815-B-19-020

18) QC TABLE

See Attachment VI

19) Revision History

v2.0
Y7BM – 01/2021

1. Updated GenX MRL to 2ng/L
2. Changed Methanol chemical grade from P&T grade to LCMS grade
3. Removed Argon from Section 6) Equipment and Supplies
4. Updated part numbers Section 6) Equipment and Supplies
5. Updated standard preparation in Section 7.11 thru 7.14
6. Added minimum scan requirement for each peak in section 11.2.4. A minimum of 10 scans across the chromatographic peak is needed to ensure adequate precision
7. Updated extraction Procedure in section 12.2.4 adding LFB/LCS—Mid/High. Corrected typo error on "Field"
8. Added Revision History in section 19
9. Updated Sections 9.4, 9.7.2, 9.8.2-9.8.4 with clearer statements on dealing with failing data and reporting
10. Updated 12.2.4 to match attachment sequence
11. Updated Attachment IV B.1 to note Genpure water (brand of system)
12. Updated Attachment IV E2, Holding time of standards from 14 days to 28 days to match extracts when CoA of vendor does not state expiration date (method does not define and only mentions stability).
13. Updated Attachment VII to note that LCSD/LFB Dup is not optional when there are AZ samples in the batch, added Cal Standard 8, and removed duplicate Cal Standard 1
14. Updated Attachment IV. Standard mix are now available from commercial vendor thus neat standards are no longer used in standard preparation. Removed standard preparation procedure from neat standards i.e. details on the weight of each neat standard is dissolved in a certain amount of MeOH

URED – 02/10/21

15. Updated Section 5 with current H&S related information
16. Updated Sections 6 and 7 with regards to critical instrumentation/supplies being available

v3.0
URED – 6/21/21

1. Corrected a typo in Section 14.1.4 to correctly reference 14.1.3
2. Updated 9.6.1 to note that CCVs are acceptable but there may be other criteria on ASM side (PA requires flagged data approval, for instance).

V4.0
URED – 11/7/22

1. Removed references to STARLIMS and webforms and replaced with TALS.
2. Removed notations on standard labeling as this is all handled within TALS.
3. Updated Attachments I, II, and III with more recent information.
4. Noted QC synonyms within TALS.

ATTACHMENTS

A. Attachment I, Documentation of Minimum Reporting Limit Study

B. Attachment II, Documentation of Method Detection Limit Study

C. Attachment III, Documentation of Demonstration of Precision and Accuracy

C. Attachment IV, Standard Preparation

D. Attachment V, Instrument Conditions

E. Attachment VI, QC Summary

F. Attachment VII, Analytical Sequence

G. Attachment VIII, Procedure for pH and Free Chlorine Checks

H. Attachment IX, Extraction Procedure

Attachment I, Documentation of Minimum Reporting Limit Study

Method:	@533
Instrument ID:	LCMS11
Date Reported	03/23/22
Units	PPT
SOP ID:	30814
SOP Revision:	1

PIR Study

Analysis Date/Time	3/23/2022 22:18	3/23/2022 22:27	3/23/2022 22:37	3/23/2022 22:46	3/23/2022 22:56	3/23/2022 23:06	3/23/2022 23:15
Extraction Date	03/22/22	03/22/22	03/22/22	03/22/22	03/22/22	03/22/22	03/22/22
Extraction Batch	1393921	1393921	1393921	1393921	1393921	1393921	1393921
LCMS Analyst	KAM	KAM	KAM	KAM	KAM	KAM	KAM
Extraction Analyst	TBS	TBS	TBS	TBS	TBS	TBS	TBS
Sample Name	202203220112	202203220113	202203220114	202203220115	202203220116	202203220117	202203220118

% Recovery Requirement	
50%	150%

Compound Name	SPIKED VALUE	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	ave	%rec	stdev	%rsd	MDL_s
11CL-PF3OUdS	2	2.019	2.085	2.02	2.031	2.031	2.031	2.074	2.041571429	102.1%	0.027	1.3%	0.084
9CI-PF3ONS	2	2.109	2.183	2.144	2.18	2.257	2.121	2.225	2.174142857	108.7%	0.054	2.5%	0.170
ADONA	2	2.287	2.26	2.2	2.223	2.175	2.343	2.413	2.271571429	113.6%	0.084	3.7%	0.264
GenX	2	2.398	2.548	2.207	2.369	2.414	2.286	2.283	2.357857143	117.9%	0.111	4.7%	0.350
PFBS	2	2.248	2.065	2.316	2.209	2.116	2.208	2.329	2.213	110.7%	0.097	4.4%	0.305
PFDA	2	2.414	2.449	2.278	2.323	2.305	2.28	2.338	2.341	117.1%	0.066	2.8%	0.208
PFDoA	2	2.192	2.284	2.221	2.229	2.328	2.131	2.288	2.239	112.0%	0.067	3.0%	0.209
PFHpA	2	2.333	2.252	2.149	2.366	2.382	2.39	2.395	2.323857143	116.2%	0.092	3.9%	0.288
PFHxA	2	2.314	2.346	2.15	2.535	2.457	2.323	2.335	2.351428571	117.6%	0.121	5.1%	0.380
PFHxS	2	2.138	2.26	2.128	2.193	2.225	2.196	2.203	2.191857143	109.6%	0.046	2.1%	0.146
PFNA	2	2.256	2.326	2.354	2.365	2.245	2.256	2.402	2.314857143	115.7%	0.063	2.7%	0.197
PFOA	2	2.503	2.404	2.241	2.418	2.404	2.312	2.471	2.393285714	119.7%	0.090	3.8%	0.283
PFOS	2	2.225	2.274	2.203	2.152	2.316	2.205	2.385	2.251428571	112.6%	0.079	3.5%	0.249
PFUnA	2	2.259	2.289	2.298	2.229	2.335	2.358	2.261	2.289857143	114.5%	0.045	2.0%	0.142
PFMBA	2	2.13	2.105	2.136	2.32	2.137	2.054	2.202	2.154857143	107.7%	0.085	3.9%	0.267
PFMPA	2	2.24	2.148	2.262	2.304	2.351	2.245	2.295	2.263571429	113.2%	0.064	2.8%	0.201
PFEESA	2	2.154	2.117	2.096	2.144	2.184	2.027	2.183	2.129285714	106.5%	0.055	2.6%	0.174
NFDHA	2	2.181	2.292	1.977	2.145	2.233	2.037	2.254	2.159857143	108.0%	0.116	5.4%	0.365
PFBA	2	2.399	2.294	2.373	2.374	2.355	2.315	2.339	2.349857143	117.5%	0.037	1.6%	0.115
PFPeA	2	2.303	2.478	2.313	2.393	2.304	2.255	2.341	2.341	117.1%	0.074	3.1%	0.231
PFPeS	2	2.219	2.155	2.105	2.272	2.177	2.099	2.293	2.188571429	109.4%	0.076	3.5%	0.240
PFHpS	2	2.218	2.395	2.229	2.185	2.329	2.121	2.338	2.259285714	113.0%	0.097	4.3%	0.306
4:2 FTS	2	2.232	2.285	2.313	2.433	2.521	2.325	2.473	2.368857143	118.4%	0.107	4.5%	0.337
6:2 FTS	2	2.282	2.486	2.348	2.427	2.409	2.251	2.482	2.383571429	119.2%	0.093	3.9%	0.292
8:2 FTS	2	2.425	2.414	2.17	2.298	2.278	2.158	2.378	2.303	115.2%	0.110	4.8%	0.345
									#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
									#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
									#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
									#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
									#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

Attachment I, Documentation of Minimum Reporting Limit Study (con't)

Method:	@533
Instrument ID:	LCMS11
Date Reported	03/23/22
Units	PPT
SOP ID:	30814
SOP Revision:	1

Compound Name	SPIKED VALUE
11CL-PF3OUdS	2
9Cl-PF3ONS	2
ADONA	2
GenX	2
PFBS	2
PFDA	2
PFDoA	2
PFHpA	2
PFHxA	2
PFHxS	2
PFNA	2
PFOA	2
PFOS	2
PFUnA	2
PFMBA	2
PFMPA	2
PFEESA	2
NFDHA	2
PFBA	2
PFPeA	2
PFPeS	2
PFHpS	2
4:2 FTS	2
6:2 FTS	2
8:2 FTS	2
0	0
0	0
0	0
0	0
0	0

Criteria:	Must be +		Must be <150	Must be >50
	MRL-MDL	HR (PIR)	Upper PIR Limit	Lower PIR Limit
	1.916	0.105	107.4	96.8
	1.830	0.214	119.4	98.0
	1.736	0.333	130.2	96.9
	1.650	0.442	140.0	95.8
	1.695	0.385	129.9	91.4
	1.792	0.262	130.2	103.9
	1.791	0.264	125.2	98.7
	1.712	0.363	134.4	98.0
	1.620	0.480	141.6	93.6
	1.854	0.183	118.8	100.4
	1.803	0.248	128.2	103.3
	1.717	0.357	137.5	101.8
	1.751	0.314	128.3	96.9
	1.858	0.179	123.4	105.5
	1.733	0.337	124.6	90.9
	1.799	0.253	125.8	100.5
	1.826	0.220	117.4	95.5
	1.635	0.460	131.0	85.0
	1.885	0.145	124.7	110.3
	1.769	0.292	131.6	102.5
	1.760	0.303	124.6	94.3
	1.694	0.385	132.2	93.7
	1.663	0.425	139.7	97.2
	1.708	0.368	137.6	100.8
	1.655	0.435	136.9	93.4
	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

Attachment II, Documentation of Method Detection Limit Study

Method:	@533
Instrument ID:	LCMS11
Date Reported	03/15/22
Units	ng/L
SOP ID:	30814
SOP Revision:	1

MDL Study

Analysis Date/Time		3/12/2022 5:18	3/12/2022 5:28	3/15/2022 7:16	3/15/2022 7:25	3/23/2022 22:18	3/23/2022 22:27	3/23/2022 22:37					
Extraction Date		03/10/22	03/10/22	03/11/22	03/11/22	03/22/22	03/22/22	03/22/22					
Extraction Batch		1392667	1392667	1392970	1392970	1393921	1393921	1393921					
LCMS Analyst		KAM	KAM	KAM	KAM	KAM	KAM	KAM					
Extraction Analyst		TBS	TBS	TBS	TBS	TBS	TBS	TBS					
Sample Name		202203100262	202203100263	202203110443	202203110444	202203220112	202203220113	202203220114					
Compound Name	Spike Value	StarLims MRL	Rep 1	Rep 2	Rep 1	Rep 2	Rep 5	Rep 6	Rep 7	ave	%rec	stdev	%rsd	MDL_s
11CL-PF3OUdS	2	2	2.04	2.109	2.204	2.125	2.019	2.085	2.02	2.086	104.3%	0.067	3.2%	0.211
9CI-PF3ONS	2	2	2.072	2.082	2.251	2.087	2.109	2.183	2.144	2.13257	106.6%	0.065	3.1%	0.205
ADONA	2	2	2.241	2.334	2.493	2.279	2.287	2.26	2.2	2.29914	115.0%	0.095	4.1%	0.298
GenX	2	5	2.379	2.289	2.677	2.251	2.398	2.548	2.207	2.39271	119.6%	0.169	7.0%	0.530
PFBS	2	2	2.372	2.292	2.387	2.297	2.248	2.065	2.316	2.28243	114.1%	0.107	4.7%	0.337
PFDA	2	2	2.225	2.197	2.348	2.207	2.414	2.449	2.278	2.30257	115.1%	0.102	4.4%	0.322
PFDoA	2	2	2.238	2.283	2.579	2.351	2.192	2.284	2.221	2.30686	115.3%	0.131	5.7%	0.411
PFHpA	2	2	2.279	2.363	2.463	2.163	2.333	2.252	2.149	2.286	114.3%	0.111	4.9%	0.350
PFHxA	2	2	2.505	2.245	2.47	2.54	2.314	2.346	2.15	2.36714	118.4%	0.144	6.1%	0.453
PFHxS	2	2	2.214	2.248	2.392	2.162	2.138	2.26	2.128	2.22029	111.0%	0.092	4.1%	0.289
PFNA	2	2	2.396	2.314	2.367	2.338	2.256	2.326	2.354	2.33586	116.8%	0.044	1.9%	0.140
PFOA	2	2	2.55	2.413	2.328	2.453	2.503	2.404	2.241	2.41314	120.7%	0.104	4.3%	0.328
PFOS	2	2	2.156	2.277	2.366	2.343	2.225	2.274	2.203	2.26343	113.2%	0.075	3.3%	0.236
PFUnA	2	2	2.225	2.282	2.326	2.18	2.259	2.289	2.298	2.26557	113.3%	0.049	2.2%	0.155
PFMBA	2	2	2.327	2.17	2.48	2.171	2.13	2.105	2.136	2.217	110.9%	0.137	6.2%	0.430
PFMPA	2	2	2.494	2.334	2.566	2.298	2.24	2.348	2.262	2.33457	116.7%	0.147	6.3%	0.461
PFEESA	2	2	2.396	2.239	2.447	2.251	2.154	2.117	2.096	2.24286	112.1%	0.136	6.1%	0.427
NFDHA	2	2	2.064	2.279	2.231	2.425	2.181	2.292	1.977	2.20614	110.3%	0.149	6.8%	0.469
PFBA	2	2	2.371	2.404	2.666	2.457	2.399	2.294	2.379	2.42343	121.2%	0.118	4.9%	0.370
PFPeA	2	2	2.439	2.39	2.56	2.614	2.303	2.478	2.313	2.44243	122.1%	0.118	4.8%	0.371
PFPeS	2	2	2.171	2.234	2.355	2.267	2.219	2.155	2.105	2.21514	110.8%	0.082	3.7%	0.258
PFHpS	2	2	2.334	2.32	2.405	2.226	2.218	2.395	2.229	2.30386	115.2%	0.080	3.5%	0.253
4:2 FTS	2	2	2.334	2.311	2.43	2.248	2.232	2.285	2.313	2.30757	115.4%	0.065	2.8%	0.205
6:2 FTS	2	2	2.423	2.323	2.458	2.252	2.282	2.486	2.348	2.36743	118.4%	0.090	3.8%	0.282
8:2 FTS	2	2	2.133	2.324	2.623	2.399	2.425	2.414	2.17	2.35543	117.8%	0.167	7.1%	0.524

Attachment II, Documentation of Method Detection Limit Study (con't)

Method:	@533
Instrument ID:	LCMS11
Date Reported	03/15/22
Units	ng/L
SOP ID:	30814
SOP Revision:	1

PFBA
PFPeA
PFPeS
PFHpS
4:2 FTS
6:2 FTS
8:2 FTS

Blank Results

	Analysis Date/Time	3/11/2022 16:35	3/11/2022 16:44	3/11/2022 16:54	3/12/2022 4:58	3/12/2022 5:09	3/15/2022 7:06	3/15/2022 7:55
	Extraction Date	03/09/22	03/09/22	03/09/22	03/10/22	03/10/22	03/11/22	03/11/22
	Extraction Batch	1391889	1391889	1391889	1392667	1392667	1392970	1392970
	LCMS Analyst	KAM	KAM	KAM	KAM	KAM	KAM	KAM
	Extraction Analyst	TBS	TBS	TBS	TBS	TBS	TBS	TBS
	Sample Name	202203090494	202203090495	202203090496	202203100260	202203100261	202203110441	202203110442

MUST USE THE HIGHER OF
MDL_S (above) and MDL_B (below)

Compound Name		StarLims MRL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	ave	stdev	%rsd	MDL_{CALC}	MDL_B
11CL-PF3OUdS		2	0.03	0.025	0.011	0.01	0.007	0.018	0.012	0.01614	0.009	53.0%	0.027	0.043
9CI-PF3ONS		2	0.026	0.021	0.009	0.004	0.011	0.012	0.008	0.013	0.008	59.6%	0.024	0.037
ADONA		2	0.065	0.038	0.023	0.02	0.01	0.013	0.011	0.02571	0.020	77.1%	0.062	0.088
GenX		2	0.126	0.077	0.056	0.051	0.043	0.049	0.04	0.06314	0.030	47.9%	0.095	0.158
PFBS		2	0.117	0.097	0.048	0.034	0.025	0.05	0.098	0.067	0.036	54.0%	0.114	0.181
PFDA		2	0.079	0.07	0.072	0.049	0.062	0.067	0.058	0.06529	0.010	15.2%	0.031	0.096
PFDoA		2	0.126	0.08	0.068	0.063	0.051	0.072	0.063	0.07471	0.024	32.5%	0.076	0.151
PFHpA		2	0.152	0.108	0.102	0.075	0.113	0.057	0.101	0.10114	0.030	29.7%	0.094	0.195
PFHxA		2	0.197	0.179	0.127	0.095	0.152	0.091	0.104	0.135	0.042	31.2%	0.132	0.267
PFHxS		2	0.1	0.07	0.048	0.024	0.014	0.023	0.036	0.045	0.031	68.0%	0.096	0.141
PFNA		2	0.095	0.048	0.026	0.006	0.045	0.08	0.091	0.05586	0.034	60.7%	0.107	0.162
PFOA		2	0.292	0.245	0.235	0.245	0.108	0.011	0.236	0.196	0.099	50.6%	0.312	0.508
PFOS		2	0.085	0.115	0.107	0.078	0.073	0.098	0.093	0.09271	0.015	16.4%	0.048	0.141
PFUnA		2	0.094	0.081	0.042	0.065	0.08	0.034	0.058	0.06486	0.022	33.7%	0.069	0.133
PFMBA		2	0.07	0.052	0.029	0.036	0.018	0.04	0.053	0.04257	0.017	40.5%	0.054	0.097
PFMPA		2	0.067	0.046	0.027	0.023	0.017	0.026	0.029	0.03357	0.017	51.3%	0.054	0.088
PFEESA		2	0.115	0.087	0.04	0.024	0.02	0.015	0.019	0.04571	0.039	86.2%	0.124	0.170
NFDHA		2	0.063	0.049	0.022	0.011	0.055	0.042	0.038	0.04	0.018	45.7%	0.057	0.028
PFBA		2	0.316	0.175	0.12	0.237	0.148	0.235	0.297	0.21829	0.074	33.9%	0.233	0.451
PFPeA		2	0.414	0.257	0.289	0.312	0.257	0.202	0.32	0.293	0.067	22.7%	0.209	0.502
PFPeS		2	0.1	0.069	0.04	0.008	0.006	0.008	0.005	0.03371	0.038	112.3%	0.012	0.153
PFHpS		2	0.005	0.029	0.02	0.004	0.006	0.008	0.021	0.01329	0.010	74.5%	0.031	0.044
4:2 FTS		2	0.135	0.111	0.084	0.051	0.074	0.04	0.054	0.07843	0.034	44.0%	0.108	0.100
6:2 FTS		2	0.127	0.109	0.1	0.066	0.075	0.079	0.087	0.09186	0.021	23.3%	0.067	0.159
8:2 FTS		2	0.046	0.058	0.029	0.022	0.037	0.06	0.053	0.04357	0.015	33.7%	0.046	0.039

If BLK1 to BLK 7 are all non-zero numbers, then use MDL_{mb} value as the blank MDL (MDLB). If BLK1 to BLK7 are a mix of 0s and non-zero numbers, then use the highest MBLK as the blank MDL value.
If BLK1 to BLK7 are all 0, the MDLB does not apply (can not calculate MDL B with zero values)
True analyte MDL is the higher of MDL_S or MDL_B

Attachment III, Documentation of Demonstration of Precision and Accuracy

Method:	@533
Instrument ID:	LCMS11
Date Reported	03/15/22
Units	ng/L
SOP ID:	30814
SOP Revision:	1

IDOC

Analysis Date/Time	3/12/2022 5:48	3/12/2022 5:59	3/12/2022 6:09	3/12/2022 6:18	3/12/2022 6:28	3/12/2022 6:38	3/12/2022 6:47
Extraction Date	03/10/22	03/10/22	03/10/22	03/10/22	03/10/22	03/10/22	03/10/22
Extraction Batch	1392667	1392667	1392667	1392667	1392667	1392667	1392667
LCMS Analyst	KAM	KAM	KAM	KAM	KAM	KAM	KAM
Extraction Analyst	TBS	TBS	TBS	TBS	TBS	TBS	TBS
Sample Name	202203100264	202203100265	202203100266	202203100267	202203100268	202203100269	202203100270

Compound Name		True Value	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	AVE	AVE %Rec	Std Dev	%RSD	Criteria: Low %Rec Criteria	High %Rec Criteria	RSD Criteria (≤)
11CL-PF3OUdS		60	57.294	57.065	56.139	65.569	60.365	55.723	56.898	58.4361	97.39%	3.48297	5.96%	70%	130%	20%
9Cl-PF3ONS		60	59.453	60.244	58.788	68.192	62.296	57.941	60.611	61.075	101.79%	3.43345	5.62%	70%	130%	20%
ADONA		60	61.55	61.404	58.976	69.327	64.142	63.594	61.71	62.9576	104.93%	3.27062	5.19%	70%	130%	20%
GenX		60	63.155	60.268	60.47	63.596	63.613	57.26	63.406	61.6726	102.79%	2.42658	3.93%	70%	130%	20%
PFBS		60	57.064	61.808	58.957	70.073	64.773	62.847	61.541	62.4376	104.06%	4.20538	6.74%	70%	130%	20%
PFDA		60	59.971	61.584	61.777	67.592	61.074	59.309	61.141	61.7783	102.96%	2.71118	4.39%	70%	130%	20%
PFDoA		60	61.436	62.753	58.745	66.219	63.626	58.894	62.14	61.9733	103.29%	2.63267	4.25%	70%	130%	20%
PFHpA		60	60.461	59.158	61.598	68.519	64.922	60.843	62.75	62.6073	104.35%	3.18753	5.09%	70%	130%	20%
PFHxA		60	63.328	62.968	61.276	71.189	64.244	60.852	65.745	64.2289	107.05%	3.49443	5.44%	70%	130%	20%
PFHxS		60	60.088	62.172	60.79	67.054	62.729	60.079	61.667	62.0827	103.47%	2.41444	3.89%	70%	130%	20%
PFNA		60	60.923	60.256	58.526	70.282	61.91	62.284	62.706	62.4124	104.02%	3.7474	6.00%	70%	130%	20%
PFOA		60	59.89	60.048	61.37	64.735	63.235	62.179	62.479	61.9909	103.32%	1.72847	2.79%	70%	130%	20%
PFOS		60	60.237	61.379	59.292	70.017	64.093	58.919	61.181	62.1597	103.60%	3.86145	6.21%	70%	130%	20%
PFUnA		60	63.688	62.883	62.055	69.509	63.305	61.682	65.328	64.0643	106.77%	2.67918	4.18%	70%	130%	20%
PFMBA		60	62.569	62.62	60.705	62.786	62.502	60.005	59.948	61.5907	102.65%	1.3085	2.12%	70%	130%	20%
PFMPA		60	62.487	64.072	61.6	69.353	64.263	63.787	63.439	64.143	106.91%	2.48311	3.87%	70%	130%	20%
PFEESA		60	60.25	59.807	60.09	70.609	65.806	61.834	66.599	63.5707	105.95%	4.16391	6.55%	70%	130%	20%
NFDHA		60	55.149	67.206	56.663	67.659	51.241	63.241	60.709	60.2669	100.44%	6.22472	10.33%	70%	130%	20%
PFBA		60	58.512	62.616	60.601	67.637	63.824	61.025	62.502	62.3881	103.98%	2.87963	4.62%	70%	130%	20%
PFPeA		60	64.221	64.79	62.55	70.215	64.928	61.939	61.445	64.2983	107.16%	2.95567	4.60%	70%	130%	20%
PFPeS		60	62.907	59.235	60.716	70.257	65.573	60.85	60.952	62.9271	104.88%	3.81804	6.07%	70%	130%	20%
PFHpS		60	61.103	60.521	59.492	68.702	65.014	59.848	61.696	62.3394	103.90%	3.34664	5.37%	70%	130%	20%
4:2 FTS		60	61.949	58.662	59.313	71.595	65.857	64.252	62.621	63.4641	105.77%	4.39235	6.92%	70%	130%	20%
6:2 FTS		60	60.824	63.215	60.943	67.057	64.056	61.49	63.654	63.0341	105.06%	2.20932	3.50%	70%	130%	20%
8:2 FTS		60	58.982	63.13[illegible]	59.096	69.135	63.222	62.103	62.116	62.541	104.24%	3.39613	5.43%	70%	130%	20%

Analyzed by: [signature] Date: 5/3/22

Extracted by: [signature] for TBS Date: 5/3/22

Approved by: [signature] Date: 5/3/22

LCMS-FO-FRM25416
Ver 3.0 (01/27/20)

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Attachment IV: Standard Preparation

A. Sodium Hydroxide Solution (0.08M NaOH)

The NaOH solution is used during primary dilution of purchased neat standards to prevent esterification.

A.1 Weigh and dissolve 1.6g NaOH in 500mL Genpure water
A.2 Transfer the prepared NaOH solution into a polypropylene bottle, store at room temperature

B. Methanol: Water Solvent Mixture

An 80% Methanol/20% Water solvent mixture is used for preparing secondary dilution standards.

B.1 Combine 400mL LCMS Grade methanol and 100mL Genpure water
B.2 Transfer the prepared MeOH/Water solution into a polypropylene bottle, store at room temperature

C. High Working Standard (HWS), 250µg/L

The high working standard is prepared diluting a purchased stock standard with 80:20 Methanol/Water solution. Sodium Hydroxide is added to prevent esterification. Bring all standards to room temperature prior to use.

C.1 Add 7mL of @533-MeOH/Water Solvent Mixture, from Attachment III.B, to a VOA vial. Remove 3.2µL of the solvent mixture using a gastight syringe
C.2 To the same VOA vial, add 3.2µL of 0.08M NaOH solution from Attachment III.A.
C.3 Add 1mL of 2µg/mL EPA 533 PFC stock standard. Cap and invert several times to mix well
C.4 Transfer the prepared standard into 2mL polypropylene vial
C.5 Store refrigerated 4±2℃ for up to 6 months or stock standard expiration whichever comes first

D. Low Working Standard (LWS), 25µg/L

The low working standard (LWS) is prepared by diluting the high working standard (HWS) with 80:20 methanol/water. Bring all standards to room temperature prior to use.

D.1 Add about 8mL of @533-MeOH/Water Solvent Mixture, from Attachment III.B, to a 10mL volumetric flask.
D.2 To the same volumetric flask, 1mL of 250µg/L HWS
D.3 Add @533-MeOH/Water Solvent Mixture to 10mL mark. Cap and invert several times to mix well
D.4 Transfer the prepared standard into 2mL polypropylene vial
D.5 Store refrigerated 4±2℃ for up to 6 months or HWS standard expiration whichever comes first

E. Calibration/Continuing Calibration Standards

E.1 The calibration standard is prepared by combining LWS (or HWS) with IDA, IPS, and Methanol/Water solvent mixture to a 2mL final volume in a propylene vial. The volume of each standard and solvent mixture used is as follows:

Calibration/Continuing Calibration Standard						
Working Concentration*, (µg/L)	**Equivalent ppt conc in extract*, (ng/L)**	**Vol of 25µg/L @533-LWS**	**Vol of 250µg/L @533-HWS**	**Vol of 1000µg/L IPS**	**Vol of 500µg/L IDA**	**Vol of 80:20 MeOH/Water,**
0	0	0 µL	—	20 µL	40 µL	1940 µL
0.5 (MRL)	2 (MRL)	40 µL	—	20 µL	40 µL	1900 µL
1.25	5	—	10 µL	20 µL	40 µL	1930 µL
2.5	10	—	20 µL	20 µL	40 µL	1920 µL
5	20	—	40 µL	20 µL	40 µL	1900 µL
10	40	—	80 µL	20 µL	40 µL	1860 µL
15	60	—	120 µL	20 µL	40 µL	1820 µL
17.5	70	—	140 µL	20 µL	40 µL	1800 µL
20	80	—	160 µL	20 µL	40 µL	1780 µL
0.5 (CCL)	2 (CCL)	40 µL	—	20 µL	40 µL	1900 µL
7.5 (CCM)	30 (CCM)	—	60 µL	20 µL	40 µL	1880 µL
15 (CCH)	60 (CCH)	—	120 µL	20 µL	40 µL	1820 µL
7.5 (QCS)	30 (QCS)	—	60 µL	20 µL	40 µL	1880 µL

Notes: * Concentrations are in terms of PFOA. All IPS and IDA are at 10 µg/L (40 ng/L in extracts) except IPS-PFOS-$^{13}C_4$ at 30 µg/L (120 ng/L in extracts) and IDA-4:2 FTS-$^{13}C_2$, IDA-6:2 FTS-$^{13}C_2$ and IDA-8:2 FTS-$^{13}C_2$ at 40 µg/L (160 ng/L in extracts).

E.2 Store refrigerated 4±2℃ for up to 28 days or LWS/HWS/IPS/IDA standard expiration whichever comes first

Mathematically, mid concentration is 10µg/L. However, UCMR allows mid CCV (CCM) to be within 20% of mathematical mid concentration. 80% of 10µg/L is 8µg/L. For ease of measuring standards, CCM is prepared at 7.5µg/L.

F. Concentration conversion from salt form to acid form

If an analyte used was purchased in salt form, and the concentration must be corrected for salt content using the equation:

$$\text{Acid concentration} = \text{salt concentration} \times \frac{\text{MW acid}}{\text{MW salt}}$$

Sample calculation:

PFHpS is purchased as the sodium salt.

	CAS #	Chem Formula	MW-salt (from CoA), g/mol	MW-Acid - by Calc, g/mol	CoA conc As Salt, ug/mL	Conc As Acid by calc, ug/mL
PFHpS	21934-50-9	C7F15SO3Na	472.1	450.118	50	47.67

$$\text{PFHpS Acid concentration} = 472.1\mu g/mL \times \frac{450.118 g/mol}{472.1 g/mol}$$

$$\text{PFHpS Acid concentration} = 47.67 ug/mL$$

Attachment V: LCMS Operating Condition

Gradient

Total Time (min)	Flow Rate (mL/min)	A (%) 20mM Ammonium Acetate	B (%) Methanol
0	0.6	95	5
0.6	0.6	95	5
0.7	0.6	45	55
4.3	0.6	10	90
4.5	0.6	1	99
6.9	0.6	1	99
7.00	0.6	95	5
9.00	0.6	95	5

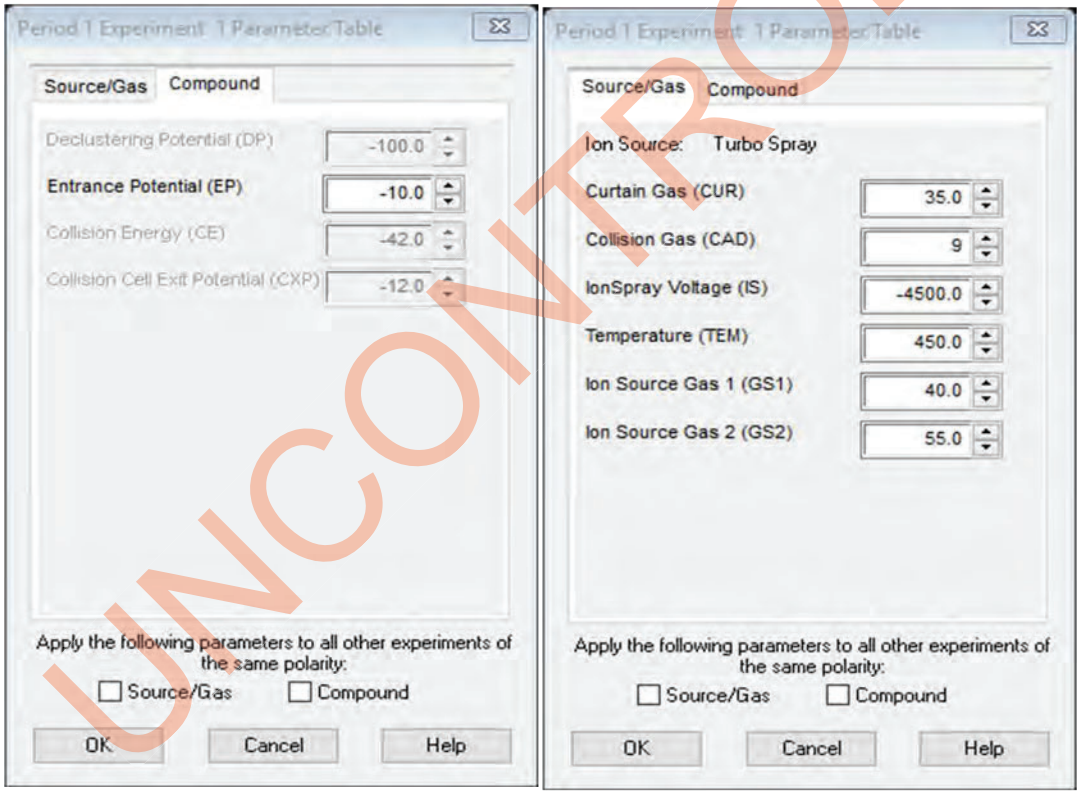
Notes: Injection Volume = 2µL (LCMS-11) and 5µL (LCMS-10), Column Temperature = 40°C, Cooler Temp = 15°C Rinse Solvent = 80% Water/20% MeOH/0.1% Formic Acid

MS/MS Parameters

Q1 Mass	Q3 Mass	RT, min	Compound	MRM Window	Dwell Weight	DP (volts)	Entrance Potential	CE (volts)	CXP (volts)
631	451	4.62	11CL-PF3OUdS		1	-100	-10	-42	-12
531	351	3.95	9Cl-PF3ONS		1	-60	-10	-40	-12
377	251	2.96	ADONA		1	-30	-10	-16	-12
285	169	2.65	GenX		1	-35	-10	-14	-12
299	80	2.24	PFBS		1	-55	-10	-58	-12
513	469	4.11	PFDA		1	-30	-10	-16	-15
613	569	4.77	PFDoA		1	-25	-10	-18	-15
363	319	2.91	PFHpA		1	-25	-10	-12	-15
313	268.8	2.53	PFHxA		1	-25	-10	-12	-15
399	80	2.92	PFHxS	75	1	-60	-10	-74	-12
463	419	3.73	PFNA		1	-25	-10	-14	-15
413	369	3.32	PFOA		1	-25	-10	-14	-15
499	80	3.72	PFOS	75	1	-65	-10	-108	-12
563	519	4.46	PFUnA		1	-25	-10	-16	-12
279	85	2.3	PFMBA		1	-20	-10	-22	-11
229	85	2.01	PFMPA		1	-15	-10	-22	-11
315	135	2.37	PFEESA		1	-75	-10	-30	-11

Q1 Mass	Q3 Mass	RT, min	Compound	MRM Window	Dwell Weight	DP (volts)	Entrance Potential	CE (volts)	CXP (volts)
295	201	2.47	NFDHA		1	-10	-10	-14	-11
213	169	1.89	PFBA		1	-25	-10	-12	-11
263	219	2.2	PFPeA		1	-20	-10	-12	-11
349	80	2.55	PFPeS		1	-100	-10	-74	-11
449	80	3.32	PFHpS		1	-65	-10	-88	-11
327	307	2.49	4:2 FTS		1	-75	-10	-28	-11
427	407	3.29	6:2 FTS		1	-50	-10	-32	-11
527	507	4.1	8:2 FTS		1	-50	-10	-40	-11
287	169	2.65	Surr-13C3-GenX		1	-35	-10	-14	-11
519	474	4.11	Surr-13C6-PFDA		1	-25	-10	-16	-11
318	273	2.53	Surr-13C5-PFHxA		1	-25	-10	-12	-11
217	172	1.89	Surr-13C4-PFBA		1	-25	-10	-12	-11
268	223	2.2	Surr-13C5-PFPeA		1	-20	-10	-12	-11
367	322	2.9	Surr-13C4-PFHpA		1	-25	-10	-12	-15
421	376	3.31	Surr-13C8-PFOA		1	-25	-10	-14	-15
472	427	3.72	Surr-13C9-PFNA		1	-25	-10	-14	-15
570	525	4.45	Surr-13C7-PFUnA		1	-25	-10	-16	-12
615	570	4.77	Surr-13C2-PFDoA		1	-25	-10	-18	-15
302	80	2.24	Surr-13C3-PFBS		1	-55	-10	-58	-12
402	80	2.91	Surr-13C3-PFHxS		1	-60	-10	-74	-12
507	80	3.72	Surr-13C8-PFOS		1	-65	-10	-108	-12
329	309	2.49	Surr-13C2-4:2 FTS		1	-75	-10	-28	-11
429	409	3.28	Surr-13C2-6:2 FTS		1	-50	-10	-32	-11
529	509	4.1	Surr-13C2-8:2 FTS		1	-50	-10	-40	-11
216	172	1.89	IS-13C3-PFBA		1	-25	-10	-12	-11
415	370	3.31	IS-13C2-PFOA		1	-25	-10	-14	-11
503	80	3.72	IS-13C4-PFOS		1	-65	-10	-108	-11

Q1 Mass	Q3 Mass	RT, min	Compound	MRM Window	Dwell Weight	DP (volts)	Entrance Potential	CE (volts)	CXP (volts)
584	419	4.39	N-EtFOSAA	75	1	-70	-10	-28	-12
570	419	4.21	N-MeTFOSAA	75	1	-70	-10	-30	-12
713	669	5.2	PFTA		1	-25	-10	-22	-15
663	619	4.96	PFTrDA		1	-25	-10	-20	-15
589.1	418.8	4.38	Surr-d5-NEtFOSAA		1	-70	-10	-30	-12
573	419	4.2	IS-d3-NMeFOSAA		1	-70	-10	-30	-12
515	470	4.04	Surr-13C2-PFDA		1	-25	-10	-16	-12
315	270	2.49	Surr-13C2-PFHxA		1	-25	-10	-12	-15
417	372	3.26	IS-13C4-PFOA		1	-25	-10	-14	-15



IPS and IDA References

No.	IPS/IDA/Analyte	Precursor Ion>Product Ion (m/z)	Reference
1	IPS-PFBA-$^{13}C_3$	216>172	None
2	IPS-PFOA-$^{13}C_2$	415>370	None
3	IPS-PFOS-$^{13}C_4$	503>80	None
4	IDA-PFBA-$^{13}C_4$	217>172	1
5	IDA-PFPeA-$^{13}C_5$	268>223	1
6	IDA-PFHxA-$^{13}C_5$	318>273	2
7	IDA-PFHpA-$^{13}C_4$	367>322	2
8	IDA-PFOA-$^{13}C_8$	421>376	2
9	IDA-PFNA-$^{13}C_9$	472>427	2
10	IDA-PFDA-$^{13}C_6$	519>474	2
11	IDA-PFUnA-$^{13}C_7$	570>525	2
12	IDA-PFDoA-$^{13}C_2$	615>570	2
13	IDA-HFPO-DA-$^{13}C_3$	287>169	2
14	IDA-PFBS-$^{13}C_3$	302>80	3
15	IDA-PFHxS-$^{13}C_3$	402>80	3
16	IDA-PFOS-$^{13}C_8$	507>80	3
17	IDA-4:2 FTS-$^{13}C_2$	329>309	3
18	IDA-6:2 FTS-$^{13}C_2$	429>409	3
19	IDA-8:2 FTS-$^{13}C_2$	529>509	3
20	PFBA	213>169	4
21	PFPeA	263>219	5
22	PFHxA	313>269	6
23	PFHpA	363>319	7
24	PFOA	413>369	8
25	PFNA	463>419	9
26	PFDA	513>469	10
27	PFUnA	563>519	11
28	PFDoA	613>569	12
29	HFPO-DA	285>169	13
30	PFBS	299>80	14
31	PFPeS	349>80	15
32	PFHxS	399>80	15
33	PFHpS	449>80	16
34	PFOS	499>80	16
35	4:2 FTS	327>307	17
36	6:2 FTS	427>407	18
37	8:2 FTS	527>507	19
38	PFMPA/PFMOPrA	229>85	4
39	PFMBA/PFMOBA	279>85	5
40	ADONA	377>251	7
41	PFEESA	315>135	14
42	NFDHA /PFMOEOAA	295>201	6
43	9Cl-PF3ONS	531>351	16
44	11Cl-PF3OUdS	631>451	16

Attachment VI, QC Summary

QC TYPE	CONCENTRATION LEVEL	FREQUENCY	ACCEPTANCE CRITERIA
Analysis Batch		Begins and ends with the appropriate CCCs. Maximum of 20 extracted field samples.	
Extraction Batch		No more than 20 field samples by the same person during a work day using the same lots of supplies.	
Initial Calibration	A minimum of 5 (linear) calibration points , the lowest must be at or lower than the MRL. Minimum 6 points required for Quadratic regression	Run during initial method set up. Run appropriate CCCs for subsequent batches, if CCCs do not meet recovery criteria, run initial calibration	Back calculate the analyte concentration and recoveries must be within 50-150% for points at or below the MRL and within 70-130% for other points.
Lab Instrument Blank (LIB)	Unextracted blank.	Optional. If analyzed, run at the beginning of the run and after the highest calibration point.	Results must be less than 1/3 the MRL.
Continuing Calibration Check (CCC)	CCL (2.0 ng/L), CCM (30 ng/L), or CCH (60 ng/L).	A CCL must be analyzed immediately after the initial calibration curve, prior to any QC or samples. Rotate CCM and CCH after every tenth field sample and at the end of each analysis batch.	Recovery must be within 50-150% of the true value for CCL and within 70-130% for CCM and CCH.
Unextracted Mid-level QCS (QCS)	30 ng/L.	Analyze as part of the IDC, at least quarterly, or with each new calibration prep.	Recovery must be within 70-130% of the true value.
Isotope Performance Standards (IPS)	40 ng/L in terms of IPS-PFOA-$^{13}C_2$.	Introduce into every field sample, calibration, and QC sample.	IPS area counts must be 50-150% of the average IS area count from the initial calibration.
Isotope Dilution Analogues (IDA)	40 ng/L in terms of IDA-PFOA-$^{13}C_8$.	Introduce into every field sample, calibration, and QC sample.	Recovery must be within 50-200% of the target value.

QC TYPE	CONCENTRATION LEVEL	FREQUENCY	ACCEPTANCE CRITERIA
Lab Reagent Blank (LRB/MBLK)	Reagent Water prepared, and analyzed as a sample.	Include one LRB with each extraction batch. If an automated system is used, the LRBs are rotated among the ports	Results must be less than 1/3 the MRL.
Lab Fortified Blank (LFB/LCS)	LFB-L (2.0 ng/L), LFB-M (30 ng/L), or LFB-H (60 ng/L).	LFB-L with each extraction batch, as well as LFB-M or LFB-H rotated.	70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Lab Fortified Sample Matrix (LFSM/MS)	Rotate between low (2.0 ng/L), mid (30 ng/L), and high (30 ng/L) between extraction batches.	Include one LFSM/MS per extraction batch (20 samples or less).	70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Lab Fortified Sample Matrix Duplicate (LFSMD/MSD)/Field Duplicate (FD/DUP)	For LFSMD, rotate between low (2.0 ng/L), mid (30 ng/L), and high (30 ng/L) between extraction batches.	Include at least one FD/DUP or LFSMD/MSD with each extraction batch.	RPD must be less than or equal to 50% for analytes within 2x the MRL. RPDs less than or equal to 30% for analytes higher than 2x the MRL. For LFSMD, 70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Field Reagent Blank (FRB)	Reagent Water prepared, and analyzed as a sample.	Process only if an associated field sample contains an analyte at or above the MRL.	Results must be less than or equal to 1/3 the MRL.
Initial Demonstration of Low System Background	Prepare, extract, and analyze as a sample.	Analyze an extracted LRB prior to any other IDC steps. If an automated system is used, the LRBs must be extracted from each port. After IDC, LRB are rotated among the ports	Results must be less than 1/3 the MRL.
Initial Demonstration of Precision	Prepare, extract and analyze 7 replicate LFB/LCSs fortified at 30 ng/L.	When beginning the use of this method, with each new analyst, and after a major change in instrumentation.	RSD must be less than 20% for the analytes.

QC TYPE	CONCENTRATION LEVEL	FREQUENCY	ACCEPTANCE CRITERIA
Initial Demonstration of Accuracy	Use the same results obtained from the Initial Demonstration of Precision.	When beginning the use of this method, with each new analyst, and after a major change in instrumentation.	Mean recovery must be within 70-130%.
Continuing Demonstration of Capability		MDL and Precision and Accuracy performed annually for each analyst or extractionist.	RSD must be less than 20% for the analytes. Mean recovery must be within 70-130%.
MRL Confirmation	Prepare, extract and analyze 7 replicate LFB/LCSs fortified at the proposed MRL.	Initially on each instrument and whenever there is a major change in instrumentation. Each new analyst and extractionist, performing this method.	The upper PIR limits must be less than or equal to 150%. The lower PIR limits must be greater than or equal to 50%.
LFB/LFBDup (LCS/LCSDup)	Rotate between mid (30 ng/L), and high (30 ng/L) between extraction batches.	For Arizona samples when MS/MSD failed acceptance for accuracy and precision	RPD must be less than or equal to 50% for analytes within 2x the MRL. RPDs less than or equal to 30% for analytes higher than 2x the MRL. 70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Establish RT for both linear and branched isomers	Run at mid to high level concentration	Run as part of IDC Repeat anytime chromatographic changes occur that alter analyte retention time.	All isomers of each analyte must elute with the same MRM window

Attachment VII, Analytical Sequence

Cal Standard 1

Cal Standard 2

Cal Standard 3

Cal Standard 4

Cal Standard 5

Cal Standard 6

Cal Standard 7

Cal Standard 8

CCC at MRL Level

QCS at Mid Level

LRB/MBLK

MRL Check

LCS/LFD

LCSD/LFB Dup (If needed, however this is not optional when there are AZ samples in the batch)

Field Sample 1

LFSM/MS on Field Sample 1

LFSMD/MSD on Field Sample 1

Field Sample 2 – 10

CCC at Mid Level

Field Sample 11 – 20

CCC at High Level

Attachment VIII, Procedure for pH and Free Chlorine Check

1) pH Check using Fisher brand pH Strips. (pH range 5 to 9)
   a) Check the pH of the samples before checking the free chlorine.
   b) Uncap the sample bottle.
   c) Using a KimWipe, wipe the mouth of the bottle every time before and after pouring out the sample. Pour 20 mL of the sample into a clean 1 ounce graduated medicine cup.
   d) Dip a pH test strip into the sample aliquot. DO NOT dip the pH test strip in the sample.
   e) Read the strip after the manufacturer's allotted development time (immediately for the Fisher brand strips). Compare the color of the paper to the corresponding color on the chart furnished with the paper. (The pH must be between 6.5 and 7.5.)
   f) Record the pH first in TALS as the original observation, and then record the pH on the sample bottle label. Mark with an "X" and set aside samples that failed to meet pH acceptance criteria for later pH verification using VWR pH strips. (pH range 6 to 10)
2) Free Chlorine Check by using SenSafe Strips
   a) Using the same 20mL aliquot that is already in the medicine cup that was used for pH as in step 1, take 1 SenSafe Strip and stroke it 40 times for 20 seconds in the sample, making 1 back stroke and 1 forth stroke per second. Make sure to keep the indicator window portion of the strip completely submerged in the sample during the 20 seconds.
   b) Record the residual chlorine result first in TALS as the original observation, and then record the residual chlorine result on the sample bottle label.

   If free chlorine is ≥ 0.1mg/L, analyst must notify ASM and generate NCM.

Attachment IX. Extraction Procedure

12) PROCEDURE

A. This procedure shall be performed using an SPE delivery apparatus device. Extraction and/or elution steps must not be changed or omitted to accommodate the use of an automated system. If an automated system is used, the LRBs must be rotated among the ports during routine analysis to ensure that all the valves and tubing meet the LRB requirements. Acceptable performance for the LRB must be met for each port during the IDC.

B. Some of the PFAS adsorb to surfaces, including polypropylene. Therefore, the aqueous sample bottles must be rinsed with the elution solvent whether extractions are performed manually or by automation. The bottle rinse is passed through the cartridge to elute the method analytes and is then collected.

C. The SPE cartridges and sample bottles described in this section are designed as single use items and shall be discarded after use. They may not be refurbished for reuse in subsequent analyses.

D. SAMPLE PREPARATION – Within 3 days of sample receipt, verify free chlorine. Verify pH prior to extraction

1. Verify and record that the sample pH is between 6.0 and 8.0. Acetic acid may be added as needed to lower the pH. If the pH is adjusted, generate a NCM to document the addition of acetic acid to the sample.
2. Verify and record that the sample has free chlorine less than 0.10 ppm. Generate a NCM if free chlorine is greater than 0.10 ppm. Notify ASM but proceed with extraction unless advised to cancel analysis.
3. Weigh and record the initial sample bottle weight to the nearest 0.5 g. After extraction, the empty bottle is also weighed. The weights are used for initial sample volume determination. Some of the PFAS adsorb to surfaces, thus the sample volume may NOT be transferred to a graduated cylinder for volume measurement.
4. The QC samples may be prepared by measuring 250 mL of reagent water with a polypropylene graduated cylinder or filling a 250 mL sample bottle to near the top. Verify and record the pH and free chlorine of all the QC samples
5. Record the spiking standards used for each batch.
6. Fortify the QC and samples with 10 µL of 1ppm isotope dilution analogue spiking standard. Cap and invert to mix. Each extraction batch must have an MRL spiked at the low level. The LCS/LCSD must be spiked at mid and high levels, which are alternated between batches. The MS/MSD must be spiked at low, mid and high levels, which are also alternated between batches. See table below for spiking amounts and spiking standards.

QC Sample	25 ppb Low Working Standard	250 ppb High Working Standard	Final Concentration in 250 mL sample
MRL	20 µL		2 ng/L
LCS/LCSD – mid level		30 µL	30 ng/L
LCS/LCSD – high level		60 µL	60 ng/L
MS/MSD – low level	20 µL		2 ng/L
MS/MSD – mid level		30 µL	30 ng/L
MS/MSD – high level		60 µL	60 ng/L

Spiking Standard	Amount Spiked	Final Concentration
0.5 ppm IDA	20 µL	40ng/L (160ng/L of telomere sulfonates) in 250 mL sample
1 ppm IPS	10 µL	10µg/L (30µg/L 13C4-PFOS) in 1 mL extract

MANUAL EXTRACTION –

APPARATUS

A. Solid Phase Extraction (SPE) Apparatus
   1. Vacuum Extraction Manifold: Equipped with flow/vacuum control
   2. Sample Delivery System: Use of polypropylene transfer lines, which transfers the sample directly from the sample container to the SPE cartridge, is recommended
   3. Laboratory Vacuum System: Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury

CARTRIDGE SPE PROCEDURE

A. Rinse the polypropylene transfer lines with methanol and then reagent water.

B. CARTRIDGE CLEAN-UP and CONDITIONING – DO NOT allow cartridge packing material to go dry during any of the conditioning steps. If the cartridge goes dry during the conditioning phase, the conditioning must be started over.
   1. Rinse each cartridge with three 5 mL aliquots of methanol. A total 15 mL of methanol.

2. Rinse each cartridge with one 5 mL aliquot of aqueous 0.10 M phosphate buffer pH 7.
3. Condition each cartridge with two 5 mL aliquots of aqueous 0.10 M phosphate buffer pH 7, without allowing the buffer solution to drop below the top edge of the packaging. A total of 10 mL of phosphate buffer solution.
4. Add 3 mL of phosphate buffer to each cartridge and fill the remaining volume with reagent water, approximately 2mL.

C. SAMPLE EXTRACTION
1. Attach a polypropylene transfer line to each cartridge.
2. Turn on the vacuum and adjust it to approximately -5 inches Hg.
3. Begin transferring the sample to the cartridge at a flow rate of about 5 mL/min. Do not allow the cartridge to go dry before all the sample has passed through. The transferring step should take approximately 50 minutes. Flow rates above 5 mL/min during transferring may cause low analyte recovery.

D. SAMPLE BOTTLE and CARTRIDGE RINSE
1. After the entire sample has passed through the cartridge, rinse the sample bottles with a 10 mL aliquot of 1 g/L ammonium acetate in reagent water. Draw the rinsate through the sample transfer lines and the cartridges.
2. Add 1 mL of methanol to the sample bottle and draw through the sample transfer lines and the cartridges. This step is designed to remove the water from the transfer lines and cartridges to reduce the salt and water present in the eluate. The methanol rinse can also help to reduce interferences by removing weakly retained organic material prior to elution.
3. Draw air through the cartridge for 10 minutes at high vacuum (15 – 20 in. Hg).

E. SAMPLE BOTTLE and CARTRIDGE ELUTION
1. Turn off and release the vacuum.
2. Lift the extraction manifold top and insert a rack with labeled collection tubes into the extraction tank to collect the extracts as they are eluted from the cartridges.
3. Rinse the sample bottles with 5 mL of methanol with 2% ammonium hydroxide (v/v)
4. Elute the analytes from the cartridges by pulling the 5 mL of 2% ammonium hydroxide in methanol (v/v) through the sample transfer lines and the cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion.
5. Repeat the sample bottle rinse and cartridge elution with a second 5 mL aliquot of methanol with 2% ammonium hydroxide (v/v)
6. Remove transfer lines

7. If needed, add additional 2% ammonium hydroxide in methanol (v/v) directly into cartridge and elute in a dropwise fashion. Final volume should be approximately 10 mL.
8. After elution, store samples at ≤ 6ºC until ready to concentrate.

F. EXTRACT CONCENTRATION and FINAL VOLUME
1. Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (55 – 60º C).
2. Reconstitute the extract with 990 µL of 20% reagent water in methanol (v/v)
3. Add 10 µL of the internal standard to the extract and vortex.
4. Transfer the final extract to a polypropylene autosampler vial and label with the appropriate sample number or QC.
5. Store extracts at room temperature until ready for analysis.

G. SAMPLE VOLUME DETERMINATION – Weigh and record the empty bottle to the nearest 0.5 g. This value is subtracted from the initial sample bottle weight to determine the initial sample volume. Assume a sample density of 1.0 g/L.

AUTOMATED EXTRACTION – This procedure is in development

APPARATUS

A. Solid Phase Extraction (SPE) Apparatus
1. An automatic/robotic sample preparation system (Thermo Scientific Dionex Autotrace 280 or equivalent) designed for use with SPE cartridges.
2. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system.
3. 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 LRB .

CARTRIDGE SPE PROCEDURE – The following steps are the procedure at which the autotrace is programmed for this method.

No.	Method
1	Process 6 Samples using the following method steps:
2	Condition Cartridge with 2.0 mL of P & T Methanol into solvent waste
3	Dry Cartridge with gas for 1.0 minutes
4	Condition Cartridge with 10.0 mL of P & T Methanol into solvent waste
5	Condition Cartridge with 10.0 mL of 0.1M phosphate buffer into aqueous waste
6	Condition Cartridge with 3.0 mL of 0.1M phosphate buffer into aqueous waste

7	Condition Cartridge with 5.0 mL of reagent water into aqueous waste
8 [a]	Load 340 mL of sample onto Cartridge
9	Pause and Alert operator, resume when CONTinue is pressed
10 [a, b]	Load 20.0 mL of sample onto Cartridge
11	Pause and Alert operator, resume when CONTinue is pressed
12 [a, c]	Load 10.0 mL of sample onto Cartridge
13	Dry Cartridge with gas for 15.0 minutes
14 [a. d]	Manually rinse Sample Container with 10.0 mL to collect
15 [a, d]	Manually rinse Sample Container with 10.0 mL to collect
16	Concentrate Sample with gas for 2.0 minutes
17	End

Notes: Nitrogen gas pressure is set at 10 psi.

[a] Ensure that the sample distribution line is properly placed in the sample bottle to withdraw the entire sample volume from the bottle.

[b] During Step 10, rinse the sample bottle with 10 mL of 1 g/L ammonium acetate/reagent water.

[c] During Step 12, rinse the sample bottle with 1 mL methanol.

[d] During Steps 114 and 15, rinse the sample bottle with 5 mL of 2% ammonium hydroxide (v/v)/methanol

Flow Rates	**Instrument Parameters**
Cond Flow: 5.0 mL/min	Max. Elution Vol.: 12.0 mL
Load Flow: 5.0 mL/min	Exhaust Fan On: Yes
Rinse Flow: 20.0 mL/min	Beeper On: Yes
Elute Flow: 5.0 mL/min	**Solvent Set**
Cond Air Push: 15.0 mL/min	Solvent 1: 0.1M phosphate buffer
Rinse Air Push: 20.0 mL/min	Solvent 2: P & T Methanol
Elute Air Push: 5.0 mL/min	Solvent 3: Reagent Water
SPE Parameters	Solvent 4: Not Used
Push Delay: 5 sec	Solvent 5: Not Used
Air Factor: 1.0	
Autowash Vol.: 1.00 mL	

EXTRACT CONCENTRATION and FINAL VOLUME

A. Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (55 – 60º C).
B. Reconstitute the extract with 990 µL of 20% reagent water in methanol (v/v)
C. Add 10 µL of the internal standard to the extract and vortex.

D. Transfer the final extract to a polypropylene autosampler vial and label with the appropriate sample number or QC.
E. Store extracts at room temperature until ready for analysis.

SAMPLE VOLUME DETERMINATION – Weigh and record the empty bottle to the nearest 0.5 g. This value is subtracted from the initial sample bottle weight to determine the initial sample volume. Assume a sample density of 1.0 g/L.

EUROFINS EATON ANALYTICAL, LLC
Standard Operating Procedure

EPA Method 537.1 Version 2.0 March 2020

Confidential

01) TITLE

Determination of selected per-and polyfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS).

02) SCOPE AND APPLICATION

A. This is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of selected perfluorinated alkyl acids (PFAS) in drinking water. Accuracy and precision data have been generated in reagent water, and finished ground and surface waters for the compounds listed in the table below.

Table 1. This method is applicable to the following analytes:

Analyte	Acronym	CAS #	MRL, ng/L
Method Analytes			
N-ethyl Perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	2

N-methyl Perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	2
Perfluorobutanesulfonic acid	PFBS	375-73-5	2
Perfluorodecanoic acid	PFDA	335-76-2	2
Perfluorododecanoic acid	PFDoA	307-55-1	2
Perfluoroheptanoic acid	PFHpA	375-85-9	2
Perfluorohexanesulfonic acid	PFHxS	355-46-4	2
Perfluorohexanoic acid	PFHxA	307-24-4	2
Perfluorononanoic acid	PFNA	375-95-1	2
Perfluorooctanesufonic acid	PFOS	1763-23-1	2
Perfluorooctanoic acid	PFOA	335-67-1	2
Perfluorotetradecanoic acid	PFTeDA	376-06-7	2
Perfluorotridecanoic acid	PFTrDA	72629-94-8	2
Perfluoroundecanoic acid	PFUnA	2058-94-8	2
Hexafluoropropylene oxide dimer acid	HFPO-DA / Gen-X	13252-13-6[a]	2
4, 8-dioxa-3H-Perfluorononanoic acid	ADONA	919005-14-4[b]	2
9-cholorohexadecafluoro-3-oxanone-1-sufonic acid	9Cl-PF3ONS	756426-58-1[c]	2
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9[d]	2

a. HFPO-DA is one component of the GenX processing aid technology.
b. ADONA is available as the sodium salt (no CASRN) and the ammonium salt (CASRN is 958445-448).
c. 9Cl-PF3ONS analyte is available in salt form (e.g. CASRN of potassium salt is 73606-19-6).
d. 11Cl-PF3OUdS is available in salt form (e.g. CASRN of potassium salt is 83329-89-9).

B. The Minimum Reporting Level (MRL) is the lowest analyte concentration that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method. The single laboratory lowest concentration MRL (LCMRL) is the lowest true concentration for which the future recovery is predicted to fall, with high confidence (99%), between 50 and 150% recovery. EPA's single laboratory LCMRLs for analytes in this method range from 0.53-6.3 ng/L. The procedure used to determine the LCMRL is described in section 14a of the SOP. Eurofins Eaton Analytical at Monrovia MRL check confirmation is done at 2ppt.

C. Eurofins Eaton Analytical (EEA-P) according to the EPA method will not be required to determine the LCMRL for this method, but will need to demonstrate that the MRL meets the requirements described in Section 9.2.6 of the referenced method EPA 537.1; Minimum Reporting Level Confirmation.

1. MDL studies are required annually by EEA-P following 40 CFR 136 MDL Revision 2. Detection limit is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.
2. The DL is compound dependent and is dependent on extraction efficiency, sample matrix, fortification concentration, and instrument performance.

3. This method is intended for use by analysts skilled in solid phase extractions, the operation of LC/MS/MS instruments, and the interpretation of the associated data.

D. METHOD FLEXIBILITY – In recognition of technological advances in analytical systems and techniques, the laboratory is permitted to modify the evaporation technique, separation technique, LC column, mobile phase composition, LC conditions and MS and MS/MS conditions. Changes may not be made to sample collection and preservation, the sample extraction steps, or to the quality control requirements (Section 11) of the referenced method EPA 537.1. Method modifications should be considered only to improve method performance. Modifications that are introduced in the interest of reducing cost or sample processing time, but result in poorer method performance, should not be used. **Analytes must be adequately resolved chromatographically in order to permit the mass spectrometer to dwell on a minimum number of compounds eluting within a retention time window. Instrumental sensitivity (or signal-to-noise) will decrease if too many compounds are permitted to elute within a retention time window**. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the initial demonstration of capability (IDC), verify that all Quality Control (QC) acceptance criteria in this method (Section 9)of the referenced method EPA 537.1 are met, and that acceptable method performance can be verified in a real sample matrix.

E. California State Water Resources Control Board Division of Drinking Water is requiring public drinking water systems approving USEPA Method 537.1 to analyze Perfluorinated Alkyl Substances (PFAs) in drinking water matrix.

03) METHOD SUMMARY

250-mL water sample is fortified with surrogates and passed through a solid phase extraction (SPE) cartridge containing polystyrenedivinylbenzene (SDVB) to extract the method analytes and surrogates. The compounds are eluted from the solid phase with a small amount of methanol. The extract is concentrated to dryness with nitrogen in a heated water bath, and then adjusted to a 1-mL volume with IS in 96:4% (vol/vol) methanol:water. A 2-5-µL injection is made into an LC equipped with a C_{18} column that is interfaced to an MS/MS. The analytes are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard technique. Surrogate analytes are added to all Field and QC Samples to monitor the extraction efficiency of the method analytes.

04) INTERFERENCES

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

a. NOTE: PFAS standards, extracts and samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAA 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 polypropylene containers.

B. Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. The method analytes in this method can also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc. All items such as these must be routinely demonstrated to be free from interferences (less than 1/3 the MRL for each method analyte) under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 11 of the referenced method EPA 537.1. **Subtracting blank values from sample results is not permitted.**

C. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent. Total organic carbon (TOC) is a good indicator of humic content of the sample. Under the LC conditions used during method development, matrix effects due to total organic carbon (TOC) were not observed.

D. Relatively large quantities of the preservative (Section 8) are added to sample bottles. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks (Section 11) of the referenced method EPA 537.1, particularly when new lots of reagents are acquired.

E. SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

05) SAFETY CONSIDERATIONS

A. Safety Data Sheets (SDSs) must be reviewed for information pertaining to the proper treatment and precautionary measure prior to handling any reagents. They are located in red binders in the Safety Officer's office and online.

B. Refer to the SOP "Hazardous Waste Management and Sample Disposal Procedures, Chemical Hygiene Plan" and OSHA Standard 29 CFR 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories; Final Rule for additional safety information

C. All samples, standards, and solvents used in this SOP should be treated as potential health hazards and handled with care. Chemists should consult relevant SDSs and follow laboratory safety procedures when doing extractions, preparing standard solutions, and performing the analysis.

D. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining an awareness of OSHA regulations regarding safe handling of chemicals used in this method.

E. PFOA has been described as likely to be carcinogenic to humans. Pure standard materials and stock standard solutions of these method analytes should be handled with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

06) INSTRUMENTATION/APPARATUS

M.

7) REAGENTS & STANDARDS

08) SAMPLE COLLECTION, PRESERVATION and HANDLING

A. SAMPLE BOTTLE PREPARATION

1. Samples must be collected in a 275-mL polypropylene bottle fitted with a polypropylene screw-cap (vendors refer to this as the 250-mL bottle). 250 ml sample is extracted as the extra volume is used for free chlorine and pH check.

2. The preservation reagent, listed in the table below, is added to each sample bottle as a solid prior to shipment to the field (or prior to sample collection).

Compound	Amount	Purpose
Trizma®	5.0 g/L	buffering reagent and removes free chlorine

B. SAMPLE COLLECTION

1. The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

2. Open the tap and allow the system to flush until the water temperature has stabilized (approximately 3 to 5 min). Collect samples from the flowing system.

3. Fill sample bottles, taking care not to flush out the sample preservation reagent. Samples do not need to be collected headspace free.

4. After collecting the sample, cap the bottle and agitate by hand until preservative is dissolved. Keep the sample sealed from time of collection until extraction.

C. FIELD REAGENT BLANKS (FRB)

1. A FRB must be handled along with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. At the laboratory, fill the field blank sample bottle with reagent water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (no preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FRB and pour the preserved reagent water into the empty shipped sample bottle, seal and label this bottle as the FRB. The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAS were not introduced into the sample during sample collection/handling.

2. The same batch of preservative must be used for the FRBs as for the field samples.

3. The reagent water used for the FRBs must be initially analyzed for method analytes as a LRB/MBLK and must meet the LRB/MBLK criteria prior to use. This requirement will ensure samples are not being discarded due to contaminated reagent water rather than contamination during sampling.

D. SAMPLE SHIPMENT AND STORAGE – Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be

at or below 6 °C when the samples are received at the laboratory 48 hours after sample collection. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen.

> **NOTE**: Samples that are significantly above 10° C, at the time of collection, may need to be iced or refrigerated for a period of time, in order to chill them prior to shipping. This will allow them to be shipped with sufficient ice to meet the above requirements.

E. SAMPLE DECHLORINATION AND PRESERVATION – Trizma as a buffer should bring sample pH to near 7.0 at room temperature. The pH of samples must be verified using pH paper, and the pH should be between 6.5 and 7.5. If pH does not meet acceptance criteria, sample is rejected. Free Chlorine is checked by using SenSafe Strips. If free chlorine is >0.1 mg/L, there is no need to confirm with DPD method. There is no need to add more Trizma Buffer if sample free chlorine is > 0.1 mg/L (See Attachment XI)

F. SAMPLE AND EXTRACT HOLDING TIMES – Results of the sample storage stability study indicated that all compounds listed in this method have adequate stability for 14 days when collected, preserved, shipped and stored as described in Sections 8.D. Therefore, water samples should be extracted as soon as possible but must be extracted within 14 days. Extracts must be stored at room temperature and analyzed within 28 days after extraction.

9) CALIBRATION PROCEDURE

10) ANALYTICAL PROCEDURE

F.

12) QUALITY CONTROL REQUIREMENTS

A. QC requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing Field Samples. This section describes the QC parameters, their required frequencies, and the performance criteria that must be met in order to meet EPA quality objectives. The QC criteria discussed in the following sections are summarized in Attachment VI. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

1. METHOD MODIFICATIONS – The analyst is permitted to modify LC columns, LC conditions, evaporation techniques, 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 IDC. **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.**

B. INITIAL DEMONSTRATION OF CAPABILITY – The IDC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined below.

1. INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND – Any time a new lot of SPE cartridges, solvents, centrifuge tubes, disposable pipets, and autosampler vials are used, it must be demonstrated that an LRB/MBLK is reasonably free of contamination and that the criteria are met. If an automated extraction system is used, an LRB/MBLK should be extracted on each port to ensure that all the valves and tubing are free from potential PFAS contamination. Acceptance limit is < 1/3 MRL.

2. INITIAL DEMONSTRATION OF PRECISION (IDP) – Prepare, extract, and analyze four to seven replicate LFB/LCSs fortified near the mid range of the initial calibration curve. Sample preservatives as described in Section 8 must be added to these samples. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

3. INITIAL DEMONSTRATION OF ACCURACY (IDA) – Using the same set of replicate data generated calculate average recovery. The average recovery of the replicate values must be within ± 30% of the true value.

4. INITIAL DEMONSTRATION OF PEAK ASYMMETRY FACTOR – Peak asymmetry factors must be calculated using the equation in Section 11 for the first two eluting peaks (if only two analytes are being analyzed, both must be evaluated) in a mid-level CAL standard. The peak asymmetry factors must fall in the range of 0.8 to 1.5.

5. MINIMUM REPORTING LEVEL (MRL) CONFIRMATION – 2ppt is established as an MRL for all compounds for this method based on the intended use of the method. The MRL may be established by a laboratory for their specific purpose or may be set by a regulatory agency. Establish an Initial Calibration following the procedure outlined in Section 11. The lowest CAL standard used to establish the Initial Calibration must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm the MRL following the procedure outlined below.

a. Fortify, extract, and analyze seven replicate LFB/LCSs at the proposed MRL concentration. These LFBs must contain all method preservatives described in Section 8. Calculate the mean measured concentration (*Mean*) and standard deviation for these replicates. Determine the Half Range for the prediction interval of results (HR_{PIR}) using the equation below

$$HR_{PIR}=3.963s$$

where
s = the standard deviation
3.963 = a constant value for seven replicates.[1]

b. Confirm that the upper and lower limits for the Prediction Interval of Result (*PIR* = *Mean* ± HR_{PIR}) meet the upper and lower recovery limits as shown below

The Upper PIR Limit must be =150% recovery.

$$\frac{Mean + HR_{PIR}}{FortifiedConcentration} \times 100\% \leq 150\%$$

The Lower PIR Limit must be =50% recovery.

$$\frac{Mean - HR_{PIR}}{FortifiedConcentration} \times 100\% \geq 50\%$$

c. The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above (Sect. 11). If these criteria are not met, the MRL has been set too low and must be determined again at a higher concentration.

6. CALIBRATION CONFIRMATION – Analyze a QCS as described in Section 11 to confirm the accuracy of the standards/calibration curve.

7. DETECTION LIMIT DETERMINATION – *It is required by various regulatory bodies associated with compliance monitoring. See Section 16 for 40 CFR, part 136, Appendix B, Rev 2 MDL Procedure.*

a. Replicate analyses for this procedure must be done over at least three days (i.e., both the sample extraction and the LC/MS/MS analyses must be done over at least three days). Prepare at least seven replicate LFB/LCSs at a concentration estimated to be near the DL. This concentration may be estimated by selecting a concentration at 2 5 times the noise level. The DLs in Attachment I were calculated from LFB/LCSs fortified at various concentrations as indicated in the table. The appropriate fortification concentrations will be dependent upon the sensitivity of the LC/MS/MS system used. All preservation reagents listed in Section 8 must also be added to these samples. Analyze the seven replicates through all steps.

NOTE: If an MRL confirmation data set meets these requirements, a DL may be calculated from the MRL confirmation data, and no additional analyses are necessary.

Calculate the *MDL* using the following equation

$$DL = s \times t_{(n-1,1-a=0.99)}$$

Where:
s = standard deviation of replicate analyses
t (*n*-1, 1-a=0.99) = Student's t value for the 99% confidence level with n-1 degrees of freedom; 3.143 for n = 7.
n = number of replicates.

NOTE: Do not subtract blank values when performing DL calculations. The MDL is a statistical determination of precision only. If the DL replicates are fortified at a low enough concentration, it is likely that they will not meet the precision and accuracy criteria for CCCs, and may result in a calculated MDL that is higher than the fortified concentration. Therefore, no precision and accuracy criteria are specified.

8. If a laboratory is establishing their own MRL, the calculated MDLs should not be used as the MRL for analytes that commonly occur as background contaminants. Method analytes that are seen in the background should be reported as present in Field

Samples, only after careful evaluation of the background levels. It is recommended that a MRL be established at the mean LRB concentrations + 3s or 3 times the mean LRB/MBLK concentration, whichever is greater. This value should be calculated over a period of time, to reflect variability in the blank measurements. It is recommended that this value be used as an MRL in order to avoid reporting false positive results.

C. ONGOING QC REQUIREMENTS – This section summarizes the ongoing QC criteria that must be followed when processing and analyzing Field Samples.

1. LABORATORY REAGENT BLANK (LRB/MBLK)(MB, MBL, etc in TALS) – An LRB/MBLK is required with each extraction batch to confirm that potential background contaminants are not interfering with the identification or quantitation of method analytes. If more than 20 Field Samples are included in a batch, analyze an LRB/MBLK for every 20 samples. If the LRB/MBLK produces a peak within the retention time window of any analyte that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or other contaminants that interfere with the measurement of method analytes must be below 1/3 of the MRL. Blank contamination is estimated by extrapolation, if the concentration is below the lowest CAL standard. This extrapolation procedure is not allowed for sample results as it may not meet data quality objectives. If the method analytes are detected in the LRB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. Because background contamination is a significant problem for several method analytes, it is highly recommended that the analyst maintain a historical record of LRB data.

2. CONTINUING CALIBRATION CHECK (CCC)(CCV, CCVIS, etc in TALS) – Low-level CCC Standard is analyzed at the beginning of each analysis batch before field samples, and the recoveries shall fall within 50-150%. Mid-level CCC and high-level CCC are analyzed after every 10 Field Samples and at the end of the analysis batch. Their recoveries shall fall within 70-130%.

3. LABORATORY FORTIFIED BLANK (LFB/LCS)(LLCS, etc in TALS) – An LFB/LCS is required with each extraction batch. The fortification concentration of the LFB/LCS must be rotated between medium and high concentration from batch to batch. In addition, one LFB/LCS at low concentration must also be extracted per day. The low concentration LFB/LCS must be as near as practical to, but no more than two times, the MRL. Similarly, the high concentration LFB/LCS should be near the high end of the calibration range established during the initial calibration. Results of the low-level LFB/LCS analyses must be 50-150% of the true value. Results of the medium and high-level LFB/LCS analyses must be 70-130% of the true value. If the LFB results do not meet these criteria for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch.

4. INTERNAL STANDARDS (IS) – The analyst must monitor the peak areas of the IS(s) in all injections during each analysis day. The IS responses (peak areas) in any chromatographic run must be within 70-140% of the response in the most recent CCC and must not deviate by more than 50% from the average area measured during initial analyte calibration. If the IS areas in a chromatographic run do not meet these criteria, inject a second aliquot of that extract aliquotted into a new capped autosampler vial.

Random evaporation losses have been observed with the polypropylene caps causing high IS(s) areas.

a. If the reinjected aliquot produces an acceptable IS response, report results for that aliquot.

b. If the reinjected extract fails again, the analyst should check the calibration by reanalyzing the most recently acceptable CAL standard. If the CAL standard fails the criteria of Section 9, recalibration is in order per Section 9. If the CAL standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as suspect. Alternatively, collect a new sample and re-analyze.

5. SURROGATE RECOVERY – The SUR standard is fortified into all samples, CCCs, LRBs, LFBs, LFSMs, LFSMDs, FD, and FRB prior to extraction see attachment for concentration. It is also added to the CAL standards. The SUR is a means of assessing method performance from extraction to final chromatographic measurement. Calculate the recovery (%R) for the SUR using the following equation

$$\%R = \left(\frac{A}{B}\right) x100$$

Where:

A = calculated surrogate concentration for the QC or field sample, and

B = fortified concentration of the surrogate.

SUR recovery must be in the range of 70-130%. When SUR recovery from a sample, blank, or CCC is less than 70% or greater than 130%, check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. Correct the problem and reanalyze the extract.

a. If the extract reanalysis meets the SUR recovery criterion, report only data for the reanalyzed extract.

b. If the extract reanalysis fails the 70-130% recovery criterion, the analyst should check the calibration by injecting the last CAL standard that passed. If the CAL standard fails the criteria of this SOP, recalibration is in order. If the CAL 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 criterion, report all data for that sample as suspect/SUR recovery to inform the data user that the results are suspect due to SUR recovery. Alternatively, collect a new sample and re-analyze.

6. LABORATORY FORTIFIED SAMPLE MATRIX (LFSM/MS) – Analysis of an LFSM/MS is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. Assessment of method precision is accomplished by analysis of a Field Duplicate (FD); however, infrequent occurrence of method analytes

would hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a second LFSM/MS, or LFSMD/MSD, must be prepared, extracted, and analyzed from a duplicate of the Field Sample. Extraction batches that contain LFSMD/MSDs will not require the extraction of a FD/DUP. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, LFSM/MS data should be documented by the laboratory for all routine sample sources.

a. Within each extraction batch, a minimum of one Field Sample (FS) is fortified as an LFSM/MS. The LFSM/MS is prepared by spiking a sample with an appropriate amount of the Analyte PDS. Select a spiking concentration that is greater than or equal to the matrix background concentration, if known. Use historical data and rotate through the low, mid and high concentrations when selecting a fortifying concentration.

b. Calculate the percent recovery (%R) for each analyte using the equation

$$R = \frac{(A-B)}{C} \times 100$$

where :

A = measured concentration in the fortified sample

B = measured concentration in the unfortified sample

C = fortification concentration.

c. Analyte recoveries may exhibit matrix bias. For samples fortified at or above their native concentration, recoveries should range between 70 - 130%, except for low-level fortification near or at the MRL (within a factor of 2 times the MRL concentration) where 50-150% recoveries are acceptable. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

7. FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD/DUP or LFSMD/MSD) – Within each extraction batch, a minimum of one FD/DUP or LFSMD/MSD must be analyzed. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If method analytes are not routinely observed in Field Samples, an LFSMD/MSD should be analyzed rather than an FD. Note that field duplicates must be reported for CA samples.

a. Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2) using the equation

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} \times 100$$

b. RPDs for FDs should be ≤ 30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of 2 of the MRL. At these concentrations, FDs should have RPDs that are ≤ 50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

c. If an LFSMD is analyzed instead of a FD, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation

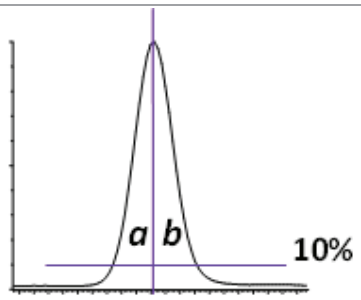
$$RPD = \left(\frac{|LFSM - LFSMD|}{(LFSM + LFSMD)/2} \right) \times 100\%$$

d. RPDs for duplicate LFSMs should be ≤ 30% for samples fortified at or above their native concentration. Greater variability may be observed when LFSMs are fortified at analyte concentrations that are within a factor of 2 of the MRL. LFSMs fortified at these concentrations should have RPDs that are ≤ 50% for samples fortified at or above their native concentration. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCC, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

8. FIELD REAGENT BLANK (FRB) or FIELD BLANK – FRB acceptance criteria is < 1/3 MRL. The purpose of the FRB is to ensure that PFAAs measured in the Field Samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the MRL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample. A FRB must have hits <= to the MRL to be considered acceptable. Samples with hits in a FRB over the MRL will invalidate the associated sample and a resample must be requested. Other QC requirements (Surrogate, internal) are identical to a typical sample. Note that, when analyzed, Field Reagent Blanks must be reported for CA samples.

TRIP BLANK - Trip blank acceptance criteria is < 1/3 MRL. This sample is to evaluate potential contamination from sample shipping and handling procedures. See section 8.G of the SOP for more details.

9. PEAK ASYMMETRY FACTOR – A peak asymmetry factor must be calculated using the equation below during the IDL and every time chromatographic changes are made that may affect peak shape. The peak asymmetry factor for the first two eluting peaks in a mid-level CAL standard (if only two analytes are being analyzed, both must be evaluated) must fall in the range of 0.8 to 1.5. **Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted.**



$A_s = \frac{b}{a}$

where:

A_S = peak asymmetry factor

b = width of the back half of the peak measured (at 10% peak height) from the trailing edge of the peak to a line dropped perpendicularly from the peak apex

a = the width of the front half of the peak measured (at 10% peak height) from the leading edge of the peak to a line dropped perpendicularly from the apex.

10. QUALITY CONTROL SAMPLES (QCS)(ICV, etc in TALS) – As part of the IDC each time a new Analyte PDS is prepared, and at least quarterly, analyze a QCS sample from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCC. Acceptance criteria for the QCS are identical to the CCCs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem.

D. Contingencies for handling out of control data or unacceptable data.

1. Submit a Non-Conformance Memo (NCM) for QC out of specification for samples that cannot be re-extracted. Generate JIRA CAR when there is a pattern or trend in the failed batch or instrument QC.
2. Details regarding use of the NCM can be found in the Absorb Training database.
3. See Policy-QA-QP3861 for a list of data qualifiers and their definitions.

E. For each batch complete a 537.1 QC Checklist

12) CALCULATIONS

A. DATA ANALYSIS AND CALCULATION

1. Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. In validating this method, concentrations were calculated by measuring the product ions. Other ions may be selected at the discretion of the analyst.

2. Calculate analyte and SUR concentrations using the multipoint calibration established. Do not use daily calibration verification data to quantitate analytes in samples. Adjust

final analyte concentrations to reflect the actual sample volume used for extraction.

3. Prior to reporting the data, the chromatogram should be reviewed for any incorrect peak identification or poor integration.

4. 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.

13) METHOD PERFORMANCE

A. Attachment I, Documentation of Demonstration of Precision and Accuracy

B. Attachment II, Documentation of Method Detection Limit Study

C. The above Attachments are current studies at the time of SOP approval only to demonstrate method performance. A more recent study is available for review upon request.

14) REFERENCES

A. EPA Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem MassSpectrometry (LC/MS/MS), Version 2.0, EPA Document No. EPA/600/R-18/352, Office of Research and Development, March 2020 .

B. EPA, EPA/815-R-05-004, Manual for the Certification of Laboratory Analyzing Drinking Water, 5th edition, January, 2005.

C. CA State Water Resources Control Board Division of Drinking Water, Drinking Water Sample Collection for Per and Polyfluorinated Alkyl Substances (PFAS) Sampling Guidance, March 2019.

D. Quality Systems for Chemical Testing. Volume 1 Module 4. 2016 TNI Standards, November 1, 2017.

E. Management and Technical Requirements for Environmental Laboratories. Volume 1 Module 2. 2016 TNI Standards, Revision 2.1, December 6, 2016.

F. US Code of Federal Regulations 40 CFR 136 MUR 2017 Appendix B-Definition and Procedure For The Determination of the Method Detection Limit Revision 2 December 2017.

15) DEVIATIONS FROM REFERENCED METHODOLOGY

A. No major deviation - using online WAX SPE as trap column for HPLC contamination control.

B. Use of a Teflon transfer tube system instead of polypropylene tube system.

C. Section 06 - Lab uses polypropylene insert in 1.8 ml amber vials instead of PP vials and caps. The method blank contamination, if any, is very negligent less than 1/3 of MRL 2 ppt.

D. For FRB, a preserved reagent water and unpreserved/empty bottle is sent to sampling site instead of Unpreserved reagent water/preserved bottle. Therefore EEA is technicaly following 537.1 rev 1 for FRB preparation due to a typo in rev 2. See Attachment XII for documentation of this issue from EPA.

16) METHOD DETECTION LIMIT

A. See section 11.B.7 of the SOP for Detection Limit Determination method requirements.

B. For general MDL procedure and requirements from 40 CFR 136, Appendix B Revision 2, see Work instructions QA-WI25066.

17) DEMONSTRATION OF CAPABILITY

A. For general Chemistry Initial and Continuing Demonstration of Capability requirements from the 2016 TNI Standard, see Work instructions QA-WI25084.

B. Refer to method specific requirements in section 11.B of the SOP for Initial Demonstration of Precision (IDP) and Initial Demonstration of Accuracy (IDA). Acceptance limits 70-130% recovery for accuracy and <20% RSD for Precision.

18) DEFINITIONS

Refer to the WI26472, Glossary for a complete list of terms and definitions.

19) POLLUTION PREVENTION

A. This method utilizes SPE to extract analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment as compared to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

B. For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036.

20) WASTE MANAGEMENT

A. It is the responsibility of the laboratory to determine whether its wastes are hazardous and to assure safe handling and disposal. The laboratory works closely with the Treatment, Storage, and Disposal Facility to ensure that certain wastes are recycled where possible, that the source of waste is reduced to the lowest possible level and that stringent land disposal restrictions are followed.

B. Refer to the following documents for additional information regarding waste management:

1. Hazardous Waste Management and Sample Disposal Procedures
2. Resource Conservation and Recovery Act (RCRA)-Title 40 of the Code of Federal Regulations, Parts 260 through 270 (40 CFR 260-270)
3. California Hazardous Waste Control Law (HWCL)-CCR Title 22 where 40 CFR was duplicated into CCR Title 22, Parts 66260-66270.

21) REVISIONS

A. Revision 1.0
New SOP

B. Revision 2.0 (EY3P 05/02/19, 05/07/19, and 05/10/19)
1. Section 8.E. - Added pH does not meet acceptance criteria, sample is rejected and updated Free Chlorine criteria.
2. Section 8.G - Removed trip blank since not required by CA
3. Section 10.C - added manual extract procedure
4. Section 11.D - Updated from a calibration curve is generated to chromatographic changes are made that may affect peak shape.
5. Section 16 - Added link to MDL requirements Work Instructions.
6. Section 17 - Added link to IDC requirements Work Instructions.
7. Added Attachment X, Procedure for pH and Free Chlorine Checks
8. All attachments - Updated header with current SOP information.
9. Section 2.C.1 - changed is to are
10. Section 9.B.1 - changed ? to to
11. Section 10.C.3 - added Automated SPE program setting
12. Section 11.B.7.a - changed ? to a

C. Revision 3.0 (KAM 07/09/19)
1. Section 9B.3 - Changed from minimum of five points calibration to six points.
2. Section 22C - update calibration table to include 60ppt in the curve.
3. Section 22C - update calibration table to include levels for CCCM and CCCH.

(ARH 12/09/19)

1. Table 1 - Corrected the name and the concentration of the following analytes - PFBS, PFHxS, Gen X, 11Cl-PF3ONS, 11Cl-PF3OUdS and PFOS.
2. Added line 7.N.4.

(Revised 12/10/19 - MFR)
1. Table 1 - Revised analyte name to match reference method. Updated MRL to 2ng/L
2. Revised Section 7 for standard preparation
3. Revised attachment table of contents, add most recent MDL and PIR study, detailed standard preparation procedure

(12/17/19 RDL)
4. Section 7.B - Replaced purified with nano-pure
5. Section 7.N.3 - Deleted "During method development, the concentrations of the SUR(s) were 10pg/µL in the standard (10ng/L in the sample) and the IS(s) were 10pg/µL. The lowest concentration CAL standard must be at or below the MRL, which may depend on system sensitivity."
6. Sections 10 -11 - Renumbered several items for clarity.

(12/17/19 MFR)
1. Section 2.C.2 Deleted "DL detection was not performed at EEA for this method"

(12/18/19 - UAON)

1. multiple sections - update from EEA to EEA-M
2. Section 6 - added " All instrumentation/apparatus listed are critical consumables for this method. Stock is kept on hand to complete analysis." as per ISO requirement
3. Section 7 - added "All reagents and standards listed are critical consumables for this method. Stock is kept on hand to complete analysis" as per ISO requirement.

Revision 4.0
(11/03/2020)

1. Changed reference to 537.1 version 2.0
2. Section 2.A table 1. Updated GenX MRL to 2ng/L
3. Added link to MSDS online
4. Updated catalog numbers on sections 6 and 7
5. Updated instrument list
6. Updated expiration of 20mM Ammonium acetate (Section 7.F)
7. Updated attachments with most recent MDL/DOC as well as added attachments XI and XII

Revision 5.0 (6/21/21 URED)
1. Updated Section 7) J. K.1., L.2., M.2., to note PDSs are good for one month.

Revision 6.0 (11/7/22 URED)
1. Updated reference links throughout the document to the new server location
2. Updated QC notations to note TALS equivalents
3. Removed STARLIMS and Webforms notations to TALS
4. Updated Attachments I, II, and III with most recent examples
5. Updated Section 9.B.2.b to note proper integration of branched isomers.
6. Updated Section 11. D. with regards to NCM use, removing QIR notations.
7. Removed references to EEA-M in Section 05)B., simply noting the SOP with a link.

22) ATTACHMENTS

A. Attachment I, Documentation of Demonstration of Method Detection Limit Study

B. Attachment II, Documentation of Demonstration of Precision and Accuracy

C. Attachment III, Documentation of Minimum Reporting Limit Study

D. Attachment IV, Standard Preparation

E. Attachment V, Instrument Conditions

F. Attachment VI, Method QC Summary

G. Attachment VII, Analytical Sequence

H. Attachment VIII, QA/QC Requirements for Method 537.1

I. Attachment IX, Caliper Lifesciences Automated SPE Workstation Conditions/Parameters

J. Attachment X, Procedure for pH and Free Chlorine Checks

K. Attachment XI, EPA email with regards to Trizma preservation

L. Attachment XII, EPA email with regards to field blanks

Attachment:
24130_537.1_attachement-v6..11.7.22.pdf (.pdf)

End of document

Version history

Version	Approval	Revision information	
4	29.DEC.2020		
5	22.JUN.2021		
6	18.JAN.2023		

ATTACHMENTS

A. Attachment I, Documentation of Method Detection Limit Study

B. Attachment II, Documentation of Demonstration of Precision and Accuracy

C. Attachment III, Documentation of Minimum Reporting Limit

D. Attachment IV, Standard Preparation

E. Attachment V, Instrument Conditions

F. Attachment VI, Method QC Summary

G. Attachment VII, Analytical Sequence

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I. Attachment IX, Caliper Lifesciences Automated SPE Workstation Conditions/Parameters

J. Attachment X, Procedure for pH and Free Chlorine Checks

K. Attachment XI, EPA email with regards to Trizma preservation

L. Attachment XII, EPA email with regards to Field Blanks

Attachment I, Documentation of Method Detection Limit Study

Method: 537.1
Instrument ID: LCMS11
Date Reported 01/28/22
Units ng/L
SOP ID: 24130
SOP Revision: 2

MDL Study

Analysis Date/Time		1/25/2022 18:34	1/25/2022 18:24	1/25/2022 18:33	1/26/2022 7:47	1/26/2022 8:56	1/27/2022 17:08	1/27/2022 17:17				
Extraction Date		01/19/22	01/19/22	01/19/22	01/21/22	01/21/22	01/26/22	01/25/22				
Extraction Batch		1380424	1380424	1380424	1381124	1381124	1381617	1381617				
LCMS Analyst		KAM	KAM	KAM	KAM	KAM	KAM	KAM				
Extraction Analyst		SV4R	SV4R	SV4R	SV4R	SV4R	SV4R	SV4R				
Sample Name		20220119l0302	20220119l0303	20220119l0304	20220121l0385	20220121l0384	20220124l0187	20220124l0188				
Compound Name	Spike Value	Stan:Lims MRL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	ave	%rec	stdev	%rsd	MDL_s
11Cl-PF3OUdS	1.884	2	1.80	1.77	1.94	1.80	1.88	1.97	1.98	1.87714	99.6%	0.088	4.7%	0.277
9Cl-PF3ONS	1.864	2	1.77	1.67	1.91	1.87	1.88	1.92	2.03	1.88429	100.0%	0.115	6.2%	0.362
ADONA	1.88	2	2.00	2.06	2.08	2.00	2.10	2.00	1.91	2.02143	107.5%	0.064	3.2%	0.202
GenX	2	2	1.89	2.09	2.22	1.99	2.16	2.12	2.19	2.09429	104.7%	0.117	5.6%	0.369
N-EtFOSAA	2	2	1.87	1.99	2.19	1.94	2.17	2.08	2.27	2.07286	103.6%	0.146	7.0%	0.459
N-MeFOSAA	2	2	1.85	1.97	2.04	1.95	2.13	2.11	2.16	2.04429	102.2%	0.090	4.4%	0.282
PFBS	1.77	2	1.88	1.86	1.94	1.94	1.93	1.93	1.98	1.92286	108.6%	0.040	2.1%	0.127
PFDA	2	2	1.98	2.03	2.07	2.04	2.07	2.11	2.16	2.06571	103.3%	0.058	2.8%	0.182
PFDoA	2	2	1.80	1.93	2.05	2.04	2.03	2.04	2.09	1.99714	99.9%	0.100	5.0%	0.313
PFHpA	2	2	2.30	2.24	2.38	2.19	2.24	2.25	2.39	2.28429	114.2%	0.076	3.3%	0.239
PFHxA	2	2	2.23	2.34	2.26	2.17	2.14	2.27	2.30	2.24429	112.2%	0.070	3.1%	0.221
PFHxS	1.824	2	1.99	1.94	1.94	1.99	2.07	2.06	2.13	2.01714	110.6%	0.072	3.5%	0.225
PFNA	2	2	1.96	2.14	2.15	2.21	2.26	2.16	2.34	2.17714	108.9%	0.121	5.6%	0.380
PFOA	2	2	2.18	2.21	2.44	2.26	2.27	2.26	2.32	2.27714	113.9%	0.085	3.7%	0.266
PFOS	1.851	6	1.76	1.90	1.96	1.84	1.97	1.94	1.91	1.9	102.6%	0.069	3.6%	0.215
PFTA	2	2	1.88	1.76	1.88	1.94	2.31	2.30	2.37	2.03429	101.7%	0.287	14.1%	0.901
PFTrDA	2	2	1.87	1.91	1.98	2.04	2.11	2.06	2.12	2.01286	100.6%	0.097	4.8%	0.303
PFUnA	2	2	1.79	1.87	2.00	1.97	1.99	1.98	2.03	1.94714	97.4%	0.085	4.4%	0.268

LCMS-FO-FRM25416
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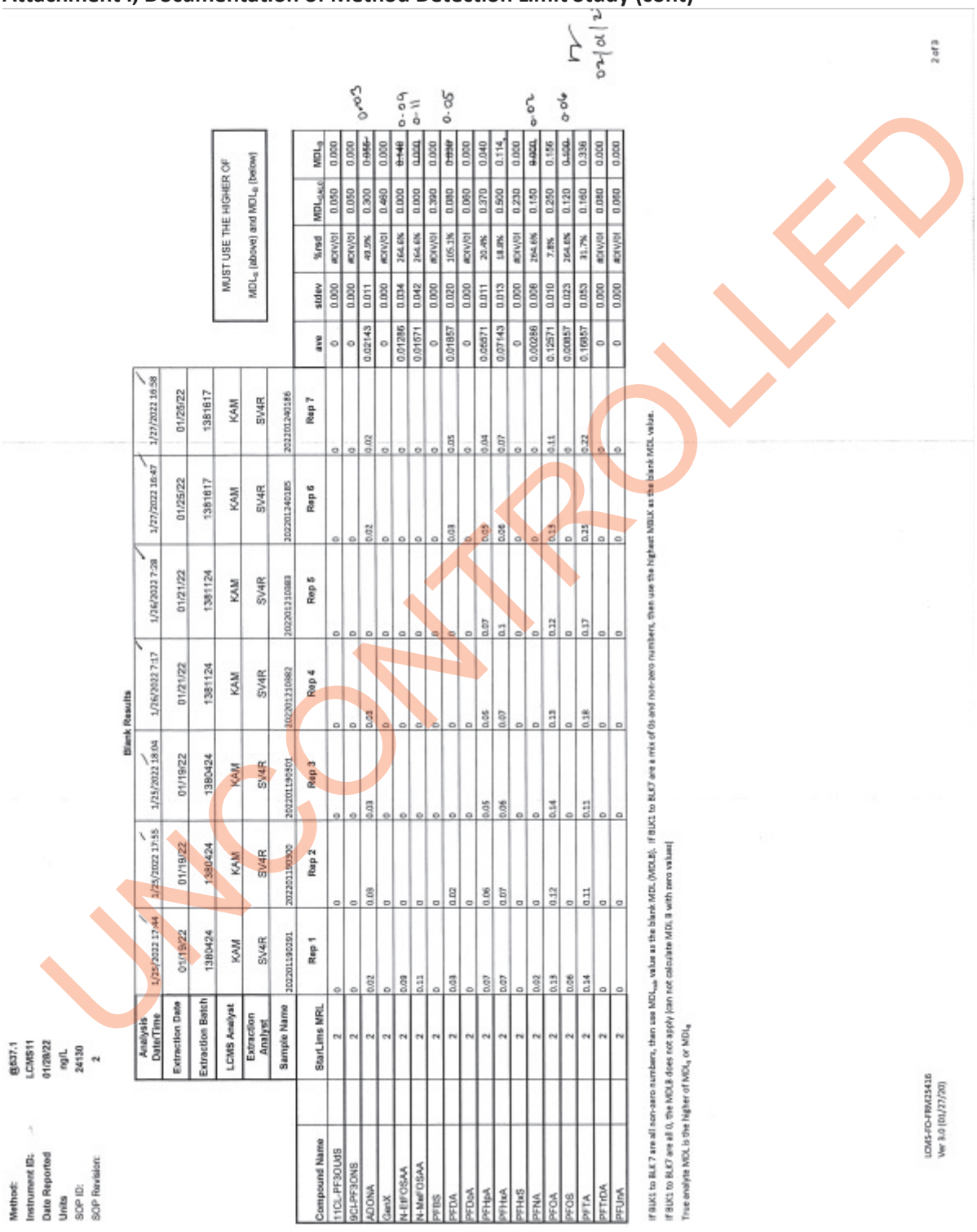
Attachment I, Documentation of Method Detection Limit Study (cont)



Method: 537.1
Instrument ID: LCMS11
Date Reported: 01/28/22
Units: ng/L
SOP ID: 24130
SOP Revision: 2

Blank Results

Analysis Date/Time		1/25/2022 17:44	1/25/2022 17:55	1/25/2022 18:04	1/26/2022 7:17	1/26/2022 7:28	1/27/2022 16:47	1/27/2022 16:58
Extraction Date		01/19/22	01/19/22	01/19/22	01/21/22	01/21/22	01/25/22	01/26/22
Extraction Batch		13804424	13804424	13804424	13811124	13811124	13811617	13811617
LCMS Analyst		KAM	KAM	KAM	KAM	KAM	KAM	KAM
Extraction Analyst		SV4R	SV4R	SV4R	SV4R	SV4R	SV4R	SV4R
Sample Name		20220111B0201	20220111B0300	20220111B0401	20220121B0882	20220121B0883	20220124B2185	20220124B2186
Compound Name	StarLims MRL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7
11Cl-PF3OUdS	2	0	0	0	0	0	0	0
9Cl-PF3ONS	2	0	0	0	0	0	0	0
ADONA	2	0.02	0.09	0.03	0.03	0	0.02	0.02
GenX	2	0	0	0	0	0	0	0
N-EtFOSAA	2	0.09	0	0	0	0	0	0
N-MeFOSAA	2	0.11	0	0	0	0	0	0
PFBS	2	0	0	0	0	0	0	0
PFDA	2	0.03	0.02	0	0	0.03	0.03	0.05
PFDoA	2	0	0	0	0	0	0	0
PFHpA	2	0.07	0.06	0.05	0.05	0.07	0.04	0.04
PFHxA	2	0.07	0.07	0.06	0.07	0.1	0.06	0.07
PFHxS	2	0	0	0	0	0	0	0
PFNA	2	0.02	0	0	0	0	0	0
PFOA	2	0.13	0.12	0.14	0.13	0.12	0.13	0.11
PFOS	2	0.06	0	0	0	0	0	0
PFTA	2	0.14	0.11	0.11	0.18	0.17	0.23	0.22
PFTrDA	2	0	0	0	0	0	0	0
PFUnA	2	0	0	0	0	0	0	0

MUST USE THE HIGHER OF MDL$_s$ (above) and MDL$_B$ (below)	ave	stdev	%rsd	MDL$_{S/B/C}$	MDL$_B$
	0	0.000	#DIV/0!	0.050	0.000
	0	0.000	#DIV/0!	0.050	0.000
	0.02143	0.011	49.9%	0.300	0.466
	0	0.000	#DIV/0!	0.460	0.000
	0.01286	0.034	264.6%	0.000	0.746
	0.01671	0.042	264.6%	0.000	0.000
	0	0.000	#DIV/0!	0.390	0.000
	0.01857	0.020	105.3%	0.080	0.000
	0	0.000	#DIV/0!	0.060	0.000
	0.05571	0.011	20.4%	0.370	0.040
	0.07143	0.013	18.8%	0.500	0.114
	0	0.000	#DIV/0!	0.230	0.000
	0.00286	0.036	264.6%	0.150	0.000
	0.12571	0.010	7.8%	0.250	0.156
	0.00857	0.023	264.6%	0.120	0.000
	0.16857	0.053	31.7%	0.160	0.336
	0	0.000	#DIV/0!	0.080	0.000
	0	0.000	#DIV/0!	0.060	0.000

0-0.03
0-0.09
0-0.11
0-0.05
0-0.07
0-0.06

If BLK1 to BLK7 are all non-zero numbers, then use MDL$_{S/B/C}$ value as the blank MDL (MDL$_B$). If BLK1 to BLK7 are a mix of 0s and non-zero numbers, then use the highest MDLK as the blank MDL value.
If BLK1 to BLK7 are all 0, the MDLB does not apply (can not calculate MDL B with zero values)
True analyte MDL is the higher of MDL$_S$ or MDL$_B$

LCMS-FD-FRM215416
Ver 3.0 (01/27/20)

2 of 3

Attachment II, Documentation of Demonstration of Precision and Accuracy

Method: 537.1
Instrument ID: LCMS11
Date Reported: 01/28/22
Units: ng/L
SOP ID: 24130
SOP Revision: 2

IDOC

Compound Name	True Value	Analysis Date/Time	1/26/2022 7:38	1/26/2022 8:19	1/26/2022 8:28	1/26/2022 8:38	1/26/2022 8:48	1/26/2022 8:57	1/26/2022 9:07			
		Extraction Date	01/21/22	01/21/22	01/21/22	01/21/22	01/21/22	01/21/22	01/21/22			
		Extraction Batch	1381124	1381124	1381124	1381124	1381124	1381124	1381124			
		LCMS Analyst	KAM	KAM	KAM	KAM	KAM	KAM	KAM			
		Extraction Analyst	SV4R	SV4R	SV4R	SV4R	SV4R	SV4R	SV4R			
		Sample Name	20220121-0386	20220121-0387	20220121-0388	20220121-0389	20220121-0390	20220121-0391	20220121-0392			
			Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	AVE	AVE %Rec	Std Dev	%RSD
11CL-PF3OUdS	23.55		17.77	22.57	21.62	21.98	22.04	22.39	22.24	21.4871	91.33%	1.66095	7.73%
9CL-PF3ONS	23.3		17.67	22.42	22.5	21.76	22.19	21.3	22.34	21.4543	92.08%	1.72192	8.03%
ADONA	23.5		18.72	23.51	23.94	23.82	24.1	23.05	23.66	22.0443	97.64%	1.89182	8.25%
GenX	25		19.17	24.63	25.18	24.05	25.23	24.38	24.62	23.8643	95.58%	2.12462	8.89%
N-EtFOSAA	25		18.34	22.87	22.93	22.49	22.72	22.75	23.69	22.2571	89.03%	1.76761	7.94%
N-MeFOSAA	25		19.48	23.98	24.53	23.87	25.2	24.12	24.58	23.9857	95.94%	1.76688	7.36%
PFBS	22.125		18.23	22.23	20.98	21.97	20.95	22.62	22.24	21.3171	96.35%	1.50486	7.06%
PFDA	25		18.87	23.28	24.45	24.08	24.61	23.86	23.79	23.26	93.12%	1.95657	8.56%
PFDoA	25		18.42	23.16	23.82	23.56	22.89	22.98	23.89	22.8486	90.59%	1.91637	8.46%
PFHpA	25		19.58	25.13	25.72	24.99	26.42	25.39	25.6	24.69	98.76%	2.301	9.32%
PFHxA	25		19.66	25.37	25.47	25.3	25.75	25.14	26.47	24.6857	98.38%	2.1847	8.88%
PFHxS	22.8		18.93	24.04	23.66	23.26	23.85	23.98	23.67	22.8986	100.87%	1.81363	7.92%
PFNA	25		19.5	24.77	25.17	24.9	25.51	24.54	24.95	24.1914	96.77%	2.09123	8.64%
PFOA	25		19.24	24.92	25.4	25.11	26.13	24.74	24.54	24.2971	97.19%	2.28982	9.42%
PFOS	23.138		18.1	22.47	22.49	22.07	22.14	22.94	22.78	21.8557	94.46%	1.68532	7.71%
PFTA	25		19.01	23.4	24.05	24.2	24.13	23.27	23.75	23.1157	92.46%	1.84577	7.98%
PFTrDA	25		18.98	23	24.29	23.24	24.62	22.96	24.02	23.0157	92.06%	1.89603	8.23%
PFUnA	25		18.4	22.38	23.29	22.84	23.61	23.09	23.67	22.46	89.84%	1.84932	8.23%

Analyzed by: Date: 2/1/22
Extracted by: Date: 2/1/22
Approved by: Date: 02/01/22

LCMS-FD-FRM25416
Ver 3.0 (03/27/20)

Attachment III, Documentation of Minimum Reporting Limit Study

Method:	@537.1
Instrument ID:	LCMS11
Date Reported	01/28/22
Units	PPT
SOP ID:	24130
SOP Revision:	2

IDOC

Compound Name	True Value	Rep 1	Rep 2	Rep 3	Rep 4	AVE	AVE %Rec	Std Dev	%RSD
	Analysis Date/Time	1/26/2022 7:38	1/26/2022 8:19	1/26/2022 8:28	1/26/2022 8:38				
	Extraction Date	1/21/2022	1/21/2022	1/21/2022	1/21/2022				
	Extraction Batch	1381124	1381124	1381124	1381124				
	LCMS Analyst	KAM	KAM	KAM	KAM				
	Extraction Analyst	SV4R	SV4R	SV4R	SV4R				
	Sample Name	202201210386	202201210387	202201210388	202201210389				
11CL-PF3OUdS	23.55	17.77	22.37	21.62	21.98	20.935	88.90%	2.132111629	10.18%
9Cl-PF3ONS	23.3	17.67	22.42	22.5	21.76	21.0875	90.50%	2.30233758	10.92%
ADONA	23.5	18.72	23.51	23.94	23.62	22.4475	95.52%	2.491684504	11.10%
GenX	25	19.17	24.63	25.18	24.05	23.2575	93.03%	2.763782131	11.88%
N-EtFOSAA	25	18.34	22.87	22.93	22.49	21.6575	86.63%	2.220230844	10.25%
N-MeFOSAA	25	19.48	23.98	24.33	23.87	22.915	91.66%	2.29838349	10.03%
PFBS	22.125	18.23	22.23	20.98	21.97	20.8525	94.25%	1.829396531	8.77%
PFDA	25	18.87	23.28	24.45	24.08	22.67	90.68%	2.57996124	11.38%
PFDoA	25	18.42	23.16	23.82	23.58	22.245	88.98%	2.564546744	11.53%
PFHpA	25	19.58	25.13	25.72	24.99	23.855	95.42%	2.867501816	12.02%
PFHxA	25	19.66	25.37	25.47	25.3	23.95	95.80%	2.860850689	11.95%
PFHxS	22.8	18.93	24.04	23.56	23.26	22.4475	98.45%	2.366901984	10.54%
PFNA	25	19.5	24.77	25.17	24.9	23.585	94.34%	2.728424454	11.57%
PFOA	25	19.24	24.92	25.4	25.11	23.6675	94.67%	2.958256215	12.50%
PFOS	23.138	18.1	22.47	22.49	22.07	21.2825	91.98%	2.130467476	10.01%
PFTA	25	19.01	23.4	24.05	24.2	22.665	90.66%	2.461280155	10.86%
PFTrDA	25	18.98	23	24.29	23.24	22.3775	89.51%	2.333243451	10.43%
PFUnA	25	18.4	22.32	23.29	22.84	21.7125	86.85%	2.243618729	10.33%
						#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
						#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
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Analyzed by: ________ Date: 2/1/22

Extracted by: ________ Date: 2/1/22

Approved by: ________ Date: 02/01/22

LCMS-FO-FRM20133
Ver 4.0 (11/12/18)

Attachment III, Documentation of Minimum Reporting Limit Study (cont)

Method:	@537.1
Instrument ID:	LCMS11
Date Reported	01/28/22
Units	PPT
SOP ID:	24130
SOP Revision:	2

Criteria:		Must be +		Must be <150	Must be >50
Compound Name	StarLims MRL	MRL-MDL	HR (PIR)	Upper PIR Limit	Lower PIR Limit
11Cl-PF3OUdS	1.884	1.673	0.266	113.3	85.0
9Cl-PF3ONS	1.864	1.581	0.357	117.0	78.7
ADONA	1.88	1.759	0.153	117.1	100.9
GenX	2	1.676	0.408	125.3	84.5
N-EtFOSAA	2	1.626	0.472	121.4	74.2
N-MeFOSAA	2	1.818	0.230	108.8	85.9
PFBS	1.77	1.669	0.127	114.3	100.0
PFDA	2	1.877	0.155	109.1	93.6
PFDoA	2	1.743	0.324	114.2	81.8
PFHpA	2	1.857	0.180	124.7	106.7
PFHxA	2	1.844	0.197	124.5	104.9
PFHxS	1.824	1.663	0.203	120.6	98.3
PFNA	2	1.659	0.430	129.0	86.1
PFOA	2	1.717	0.357	132.2	96.5
PFOS	1.851	1.674	0.223	114.5	90.5
PFTA	2	1.796	0.257	101.3	75.7
PFTrDA	2	1.856	0.181	105.9	87.7
PFUnA	2	1.784	0.272	108.7	81.5
0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
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LCMS-F3-FRM20133
Ver 4.0(11/12/18)

2 of 3

Attachment IV, Standard Preparation

A. 537 Analyte Primary Dilution Standard (PDS), high concentration

The high concentration analyte PDS solution is prepared by diluting purchased stock standard

Analyte PDS High Concentration				
Name	**Stock Standard Conc, µg/ml**	**Spike Vol**	**Final Conc, µg/ml**	**Final Vol, mL****
Custom Analyte Mix	2	3.125mL	0.25*	25

* Refer to certificate of analysis; a few analytes are less than 2µg/mL.
** A solution of 96:4 methanol/water is used to make up the remaining volume.

Bring all stock standards to room temperature before use
Transfer the prepared standard into 2mL polypropylene vials and store in the refrigerator
Record standard preparation ~~and label vials as follows @537-Analyte-PDS-STD(H)-250PPB-(DATE PREPARED)-(ANALYTS INITIALS)-(vial number)~~in TALS

B. 537 Analyte Primary Dilution Standard (PDS), low concentration

The low concentration analyte PDS solution is prepared by diluting the high concentration analyte PDS with 96:4 methanol/water

Analyte PDS Low Concentration				
Name	**PDS Standard Conc, µg/ml**	**Spike Vol, mL**	**Final Conc, µg/ml**	**Final Vol, mL***
PDS High Concentration	0.25	1	0.025	10

* A solution of 96:4 methanol/water is used to make up the remaining volume.

Bring all PDS standards to room temperature before use
Transfer the prepared standard into 2mL polypropylene vials and store in the refrigerator
Record standard preparation in TALS~~and label vials as follows @537-Analyte-PDS-STD(L)-25PPB-(DATE PREPARED)-(ANALYTS INITIALS)-(vial number)~~

Attachment IV, Standard Preparation (cont'd)

C. Calibration standard

The calibration standard is prepared as follows:

Working Conc, ug/L	Equivalent ppt Conc in Extract*	Volume of 96:4 (Methanol/water) Mixture, µL	volume 537-IS-PDS, µL	Vol 537-SURR-PDS, µL	Vol 537 PDS STD low Conc, µL	Vol 537 PDS STD High Conc, µL
0	0	1960	20	20	0	-
0.5	2	1920	20	20	40	-
1.25	5	1950	20	20	-	10
2.5	10	1940	20	20	-	20
5	20	1920	20	20	-	40
10	40	1880	20	20	-	80
15	60	1840	20	20	-	120
20	80	1800	20	20	-	160
0.5	2 = CCCL	1920	20	20	40	-
7.5	30 = CCCM	1900	20	20	-	60
12.5	50 = CCCH	1860	20	20	-	100

*This concentration incorporates sample prep factor. A 250mL sample is extracted with an extract final volume of 1mL

Bring all standards to room temperature before use
Record standard preparation ~~and label vials as follows @537-CAL-(DATE PREPARED)-(ANALYTS INITIALS)~~in TALS

Attachment IV, Standard Preparation (cont'd)

D. Second Source Primary Dilution Standard

The second source PDS solution is prepared by diluting a stock standard 96:4 methanol/water. The second source stock standard should be purchased from a vendor different from what was used in analyte PDS standard (attachment III, section A and B)

Analyte PDS Low Concentration				
Name	**PDS Standard Conc, µg/ml**	**Spike Vol, mL**	**Final Conc, µg/ml**	**Final Vol, mL***
2nd Source custom Mix	2	0.625	0.25	5

* A solution of 96:4 methanol/water is used to make up the remaining volume.

Bring stock standards to room temperature before use
Transfer the prepared standard into 2mL polypropylene vials and store in the refrigerator
Record standard preparation ~~and label vials as follows @537-QCS-PDS-(DATE PREPARED)-(ANALYTS INITIALS)-(vial number)~~in TALS.

E. Second source QCS

The second source QCS is analyzed after every calibration and is prepared by combining several standards

Working Conc, ug/L	**Equivalent ppt Conc in Extract***	**Volume of 96:4 (Methanol/water) Mixture, µL**	**volume 537-IS-PDS, µL**	**Vol 537-SURR-PDS, µL**	**Vol 2nd Source PDS, µL**
5	20	1920	20	20	40

*This concentration incorporates sample prep factor. A 250mL sample is extracted with an extract final volume of 1mL

Bring all standards to room temperature before use
Record standard preparation in TALS.~~and label vials as follows @537-2nd Source-QCS-(DATE PREPARED)-(ANALYTS INITIALS)~~

Attachment IV, Standard Preparation (cont'd)

F. Internal Standards Primary Dilution Standard (PDS):

The IS PDS solution is prepared by combining 3 separate stock standards into 1 mix

Internal Standard Preparation				
Name	**Stock Standard Conc, µg/ml**	**Spike Vol, mL**	**Final Conc, µg/ml**	**Final Vol, mL***
13C4PFOA (MPFOA)	50	0.5	1	25
13C4PFOS (MPFOS)	50	0.5	1	
d3-NMeFOSAA	50	2	4	

* A solution of 96:4 methanol/water is used to make up the remaining volume.

Bring all stock standards to room temperature before use
Transfer the prepared standard into 2mL polypropylene vials and store in the refrigerator
Record standard preparation ~~and label vials as follows @537-IS-PDS-STANDARD-(DATE PREPARED)-(ANALYTS INITIALS)-(vial number)~~in TALS.

G. 537 IS Solution

The IS solution is used at sample preparation. It is prepared by diluting @537 IS Primary Dilution Standard

a.) Add 5mL of @537-IS-PDS to a 500mL volumetric flask with about 490mL 96:4 methanol/water solution
b.) Fill to the mark with 96:4 methanol/water solution
c.) Cap and invert flask several times to mix
d.) Transfer into corning centric star vials.
e.) Record standard preparation ~~and label vials as follows @537-IS-SOLUTION-(DATE PREPARED)-(ANALYTS INITIALS)~~in TALS.
f.) Store standards in the refrigerator. Bring to room temperature prior to use

Attachment IV, Standard Preparation (cont'd)

H. Surrogate Primary Dilution Standard

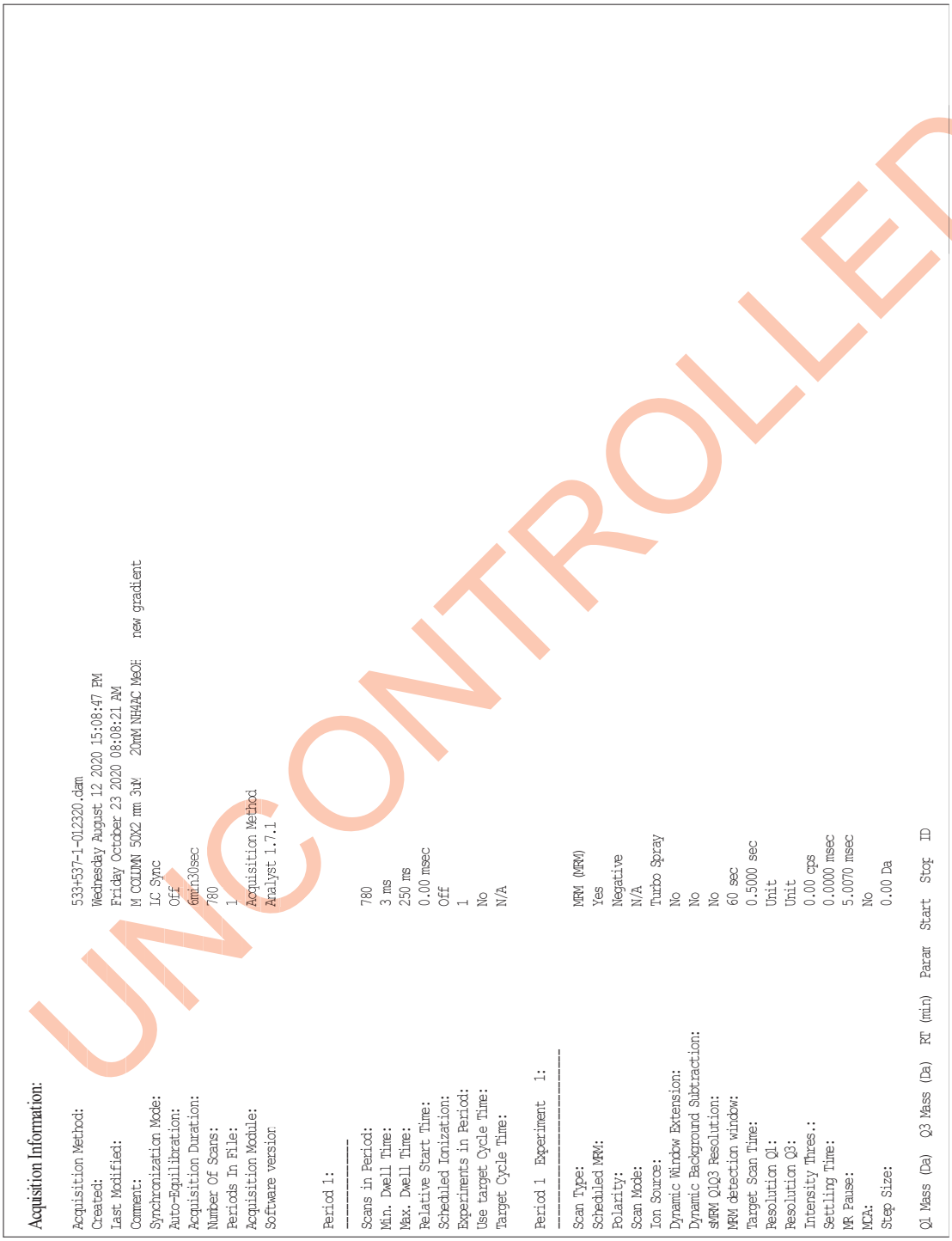
The surrogate PDS solution is prepared by combining 4 separate stock standards into 1 mix

Surrogate Standard Preparation				
Name	**Stock Conc. (µg/mL)**	**Spike Vol. (mL)**	**Surr Conc. (µg/mL)**	**Final Vol. (mL)***
13C2-PFHxA (MPHXA)	50	0.5	1	25
13C2-PFDA (MPFDA)	50	0.5	1	
d5-NEtFOSAA	50	2	4	
GenX-13C3 (M3HFPO-DA)	50	0.5	1	

* A solution of 96:4 methanol/water is used to make up the remaining volume.

Bring all stock standards to room temperature before use
Record standard preparation in TALS.~~and label vials as follows @537-SURR-PDS-STD-(DATE PREPARED)-(ANALYTS INITIALS)~~

Attachment V: Instrument Conditions-p1



Acquisition Information:

Acquisition Method:	533+537-1-012320.dam
Created:	Wednesday August 12 2020 15:08:47 PM
Last Modified:	Friday October 23 2020 08:08:21 AM
Comment:	M COLUMN 50X2 mm 3uM 20mM NH4AC MeOH new gradient
Synchronization Mode:	LC Sync
Auto-Equilibration:	Off
Acquisition Duration:	6min30sec
Number Of Scans:	780
Periods In File:	1
Acquisition Module:	Acquisition Method
Software version	Analyst 1.7.1

Period 1:

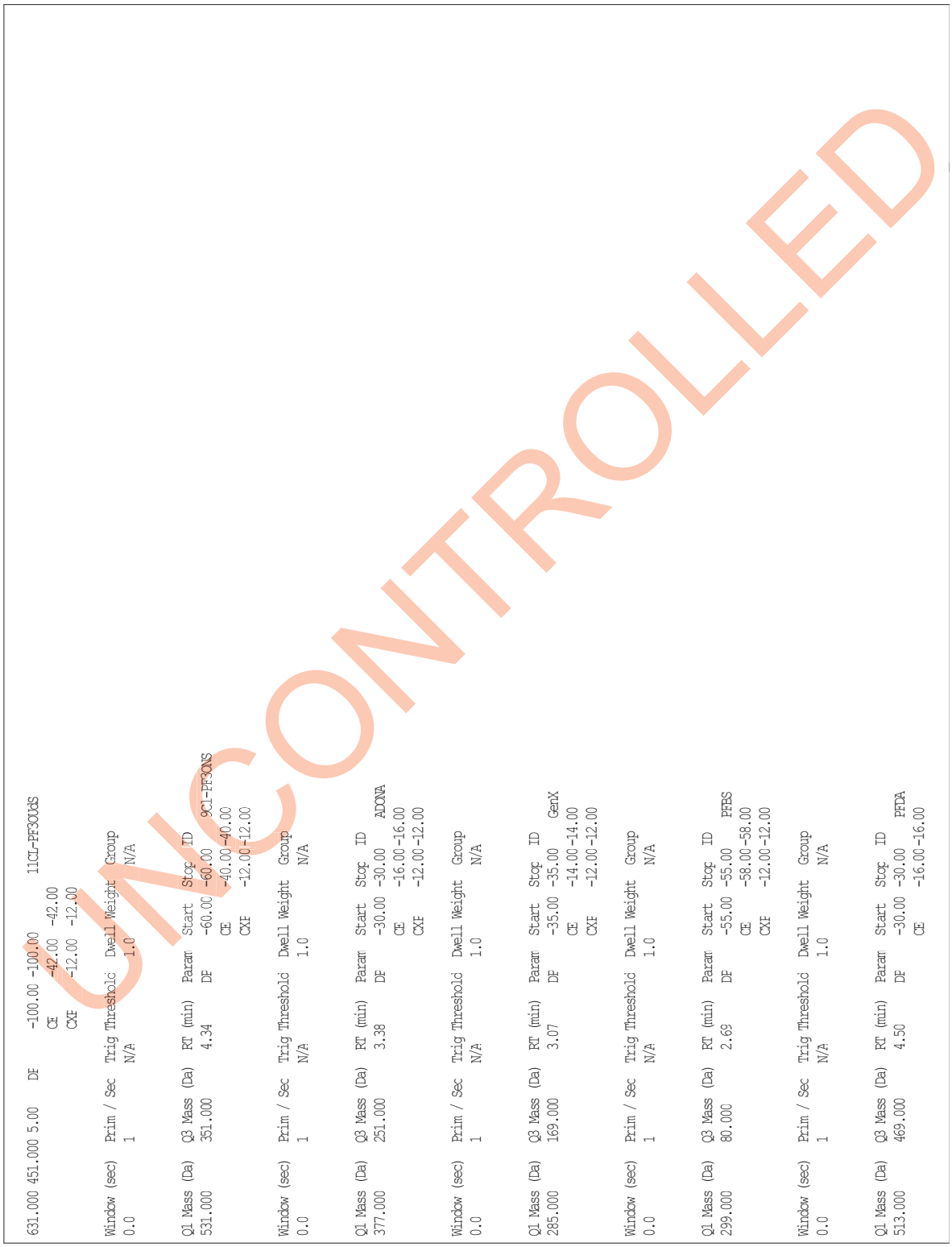
Scans in Period:	780
Min. Dwell Time:	3 ms
Max. Dwell Time:	250 ms
Relative Start Time:	0.00 msec
Scheduled Ionization:	Off
Experiments in Period:	1
Use target Cycle Time:	No
Target Cycle Time:	N/A

Period 1 Experiment 1:

Scan Type:	MRM (MRM)
Scheduled MRM:	Yes
Polarity:	Negative
Scan Mode:	N/A
Ion Source:	Turbo Spray
Dynamic Window Extension:	No
Dynamic Background Subtraction:	No
sMRM Q1Q3 Resolution:	No
MRM detection window:	60 sec
Target Scan Time:	0.5000 sec
Resolution Q1:	Unit
Resolution Q3:	Unit
Intensity Thres.:	0.00 cps
Settling Time:	0.0000 msec
MR Pause:	5.0070 msec
MCA:	No
Step Size:	0.00 Da

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID

Attachment V: Instrument Conditions (cont'd)-p2



631.000 451.000 5.00 DP -100.00 -100.00 11CL-PF3OUdS
CE -42.00 -42.00
CXP -12.00 -12.00

Window (sec) Prim / Sec Trig Threshold Dwell Weight Group
0.0 1 N/A 1.0 N/A

Q1 Mass (Da) Q3 Mass (Da) RT (min) Param Start Stoc ID 9CL-PF3ONS
531.000 351.000 4.34 DP -60.00 -60.00
CE -40.00 -40.00
CXP -12.00 -12.00

Window (sec) Prim / Sec Trig Threshold Dwell Weight Group
0.0 1 N/A 1.0 N/A

Q1 Mass (Da) Q3 Mass (Da) RT (min) Param Start Stoc ID ADONA
377.000 251.000 3.38 DP -30.00 -30.00
CE -16.00 -16.00
CXP -12.00 -12.00

Window (sec) Prim / Sec Trig Threshold Dwell Weight Group
0.0 1 N/A 1.0 N/A

Q1 Mass (Da) Q3 Mass (Da) RT (min) Param Start Stoc ID GenX
285.000 169.000 3.07 DP -35.00 -35.00
CE -14.00 -14.00
CXP -12.00 -12.00

Window (sec) Prim / Sec Trig Threshold Dwell Weight Group
0.0 1 N/A 1.0 N/A

Q1 Mass (Da) Q3 Mass (Da) RT (min) Param Start Stoc ID PFBS
299.000 80.000 2.69 DP -55.00 -55.00
CE -58.00 -58.00
CXP -12.00 -12.00

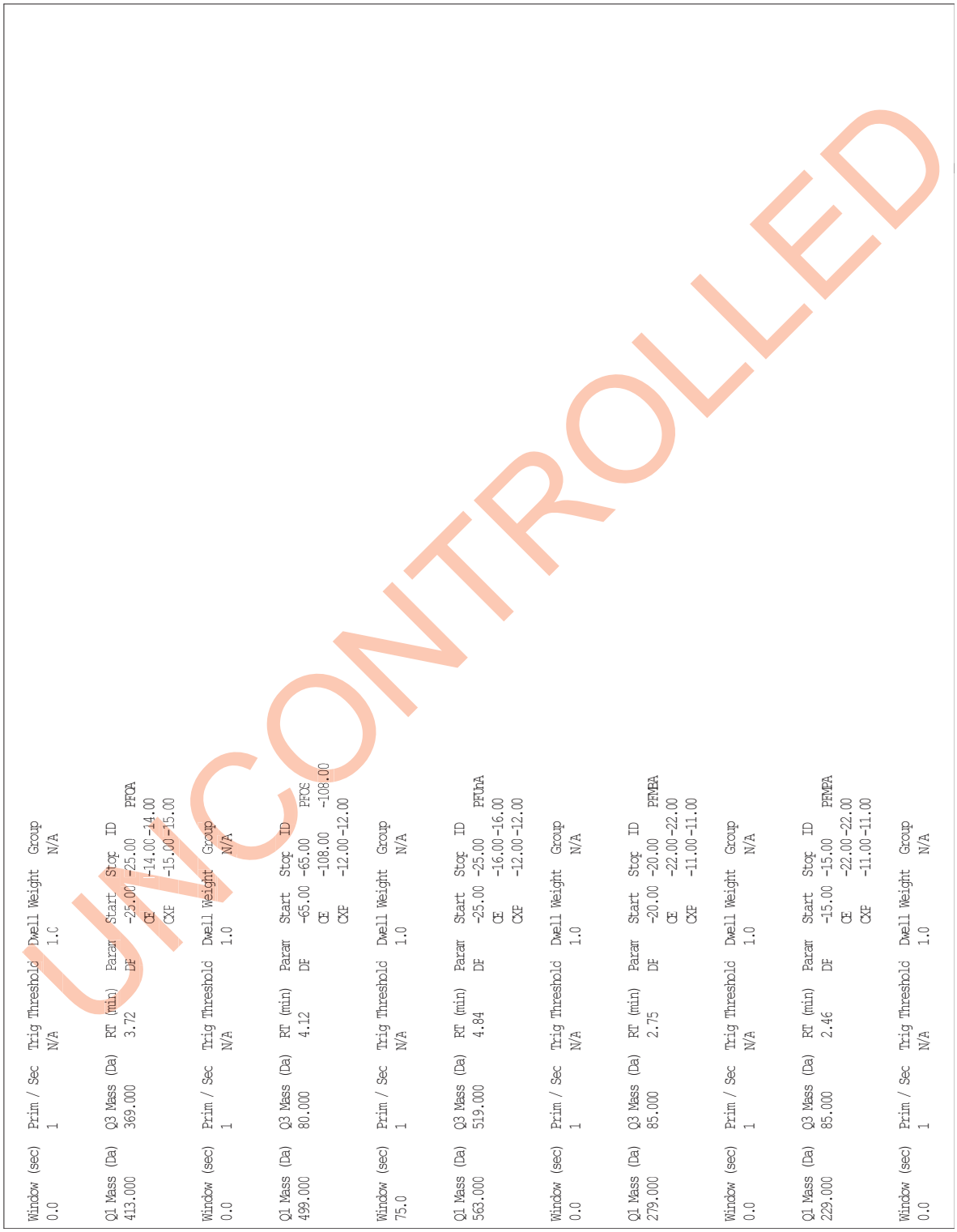
Window (sec) Prim / Sec Trig Threshold Dwell Weight Group
0.0 1 N/A 1.0 N/A

Q1 Mass (Da) Q3 Mass (Da) RT (min) Param Start Stoc ID PFDA
513.000 469.000 4.50 DP -30.00 -30.00
CE -16.00 -16.00

Attachment V: Instrument Conditions (cont'd)-p3

	CXF	-15.00	-15.00						
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
613.000	569.000	5.15	DF	-25.00	-25.00	PFDoA			
			CE	-18.00	-18.00				
			CXF	-15.00	-15.00				
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
363.000	319.000	3.33	DF	-25.00	-25.00	PFHpA			
			CE	-12.00	-12.00				
			CXF	-15.00	-15.00				
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
313.000	268.800	2.97	DF	-25.00	-25.00	PFHxA			
			CE	-12.00	-12.00				
			CXF	-15.00	-15.00				
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
399.000	80.000	3.35	DF	-60.00	-60.00	PFHxS			
			CE	-74.00	-74.00				
			CXF	-12.00	-12.00				
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
75.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
463.000	419.000	4.12	DF	-25.00	-25.00	PFNA			
			CE	-14.00	-14.00				
			CXF	-15.00	-15.00				

Attachment V: Instrument Conditions (cont'd)-p4



Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
413.000	369.000	3.72	DP	-25.00	-25.00	PFOA
			CE		-14.00	-14.00
			CXP		-15.00	-15.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
499.000	80.000	4.12	DP	-65.00	-65.00	PFOS
			CE		-108.00	-108.00
			CXP		-12.00	-12.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
75.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
563.000	519.000	4.84	DP	-25.00	-25.00	PFUnA
			CE		-16.00	-16.00
			CXP		-12.00	-12.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
279.000	85.000	2.75	DP	-20.00	-20.00	PFHxA
			CE		-22.00	-22.00
			CXP		-11.00	-11.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
229.000	85.000	2.46	DP	-15.00	-15.00	PFPeA
			CE		-22.00	-22.00
			CXP		-11.00	-11.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Attachment V: Instrument Conditions (cont'd)-p5

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
315.000	135.000	2.82	DP	-75.00	-75.00	PFEESA
			CE	-30.00	-30.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
295.000	201.000	2.93	DP	-10.00	-10.00	NFDHA
			CE	-14.00	-14.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
213.000	169.000	2.35	DP	-25.00	-25.00	PFBA
			CE	-12.00	-12.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
263.000	219.000	2.65	DP	-20.00	-20.00	PFPeA
			CE	-12.00	-12.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

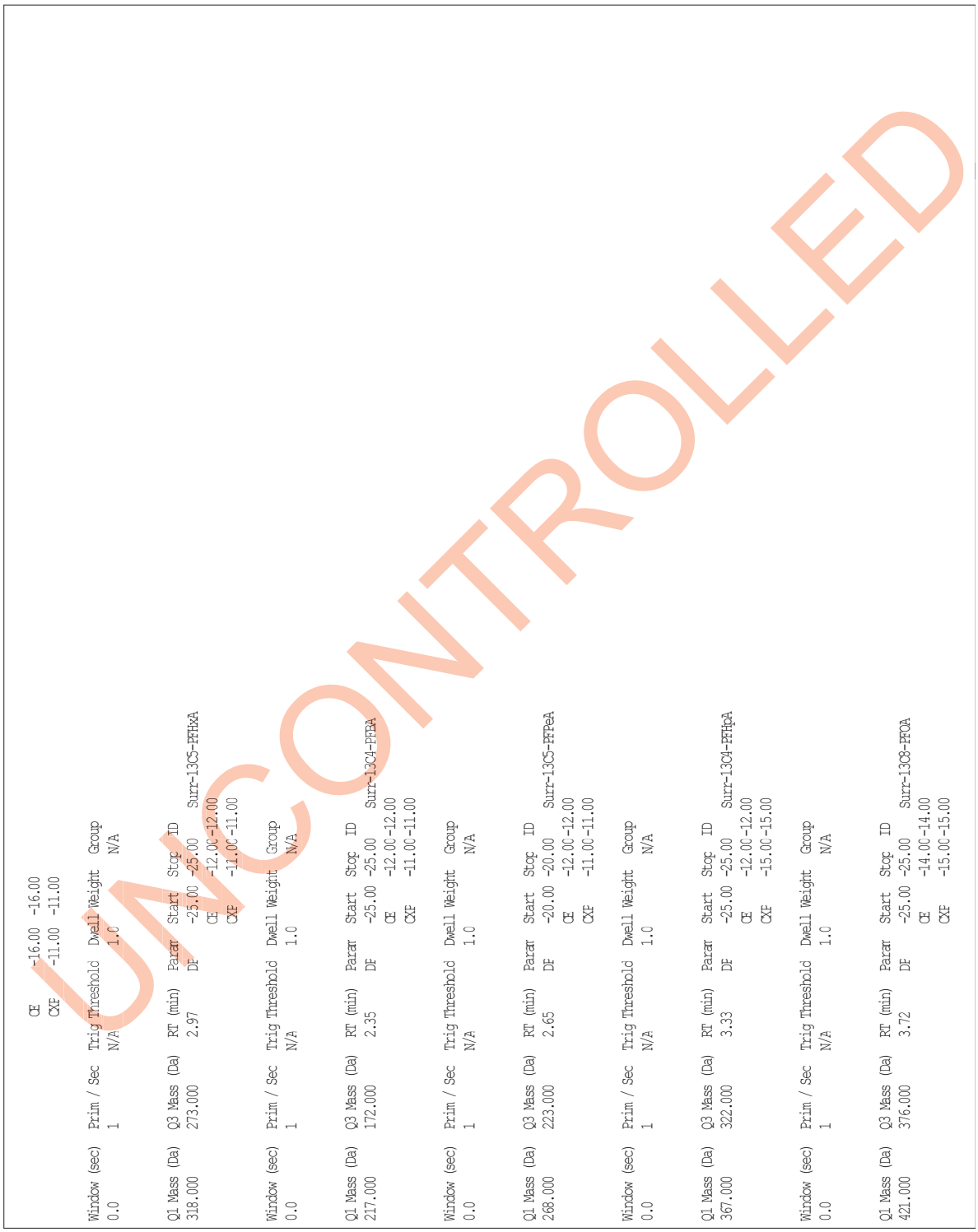
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
349.000	80.000	3.00	DP	-100.00	-100.00	PFPeS
			CE	-74.00	-74.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Attachment V: Instrument Conditions (cont'd)-p6

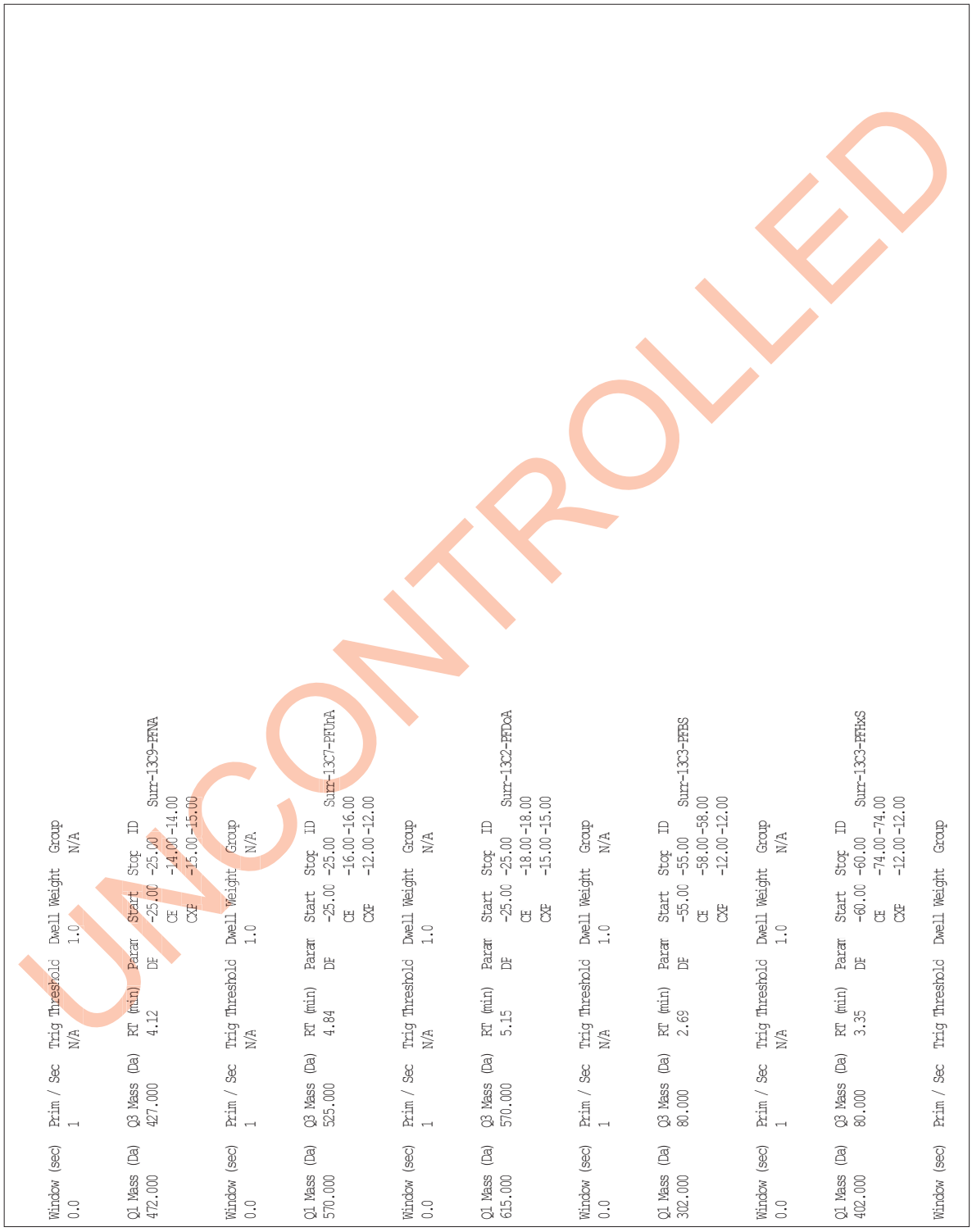
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
449.000	80.000	3.74	DF	-65.00	-65.00	PFHpS
			CE	-88.00	-88.00	
			CXF	-11.00	-11.00	
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group		
0.0	1	N/A	1.0	N/A		
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
327.000	307.000	2.95	DF	-75.00	-75.00	4:2 FTS
			CE	-28.00	-28.00	
			CXF	-11.00	-11.00	
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group		
0.0	1	N/A	1.0	N/A		
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
427.000	407.000	3.70	DF	-50.00	-50.00	6:2 FTS
			CE	-32.00	-32.00	
			CXF	-11.00	-11.00	
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group		
0.0	1	N/A	1.0	N/A		
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
527.000	507.000	4.50	DF	-50.00	-50.00	8:2 FTS
			CE	-40.00	-40.00	
			CXF	-11.00	-11.00	
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group		
0.0	1	N/A	1.0	N/A		
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
287.000	169.000	3.08	DF	-35.00	-35.00	Surr-13C3-GenX
			CE	-14.00	-14.00	
			CXF	-11.00	-11.00	
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group		
0.0	1	N/A	1.0	N/A		
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
519.000	474.000	4.50	DF	-25.00	-25.00	Surr-13C6-PFDA

Attachment V: Instrument Conditions (cont'd)-p7



	CE	-16.00	-16.00						
	CXE	-11.00	-11.00						
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
318.000	273.000	2.97	DF	-25.00	-25.00	Surr-13C5-PFHxA			
			CE		-12.00	-12.00			
			CXE		-11.00	-11.00			
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
217.000	172.000	2.35	DF	-25.00	-25.00	Surr-13C4-PFBA			
			CE		-12.00	-12.00			
			CXE		-11.00	-11.00			
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
268.000	223.000	2.65	DF	-20.00	-20.00	Surr-13C5-PFPeA			
			CE		-12.00	-12.00			
			CXE		-11.00	-11.00			
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
367.000	322.000	3.33	DF	-25.00	-25.00	Surr-13C4-PFHpA			
			CE		-12.00	-12.00			
			CXE		-15.00	-15.00			
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group					
0.0	1	N/A	1.0	N/A					
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID			
421.000	376.000	3.72	DF	-25.00	-25.00	Surr-13C8-PFOA			
			CE		-14.00	-14.00			
			CXE		-15.00	-15.00			

Attachment V: Instrument Conditions (cont'd)-p8



Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
472.000	427.000	4.12	DF	-25.00	-25.00	Surr-13C9-PFNA
			CE		-14.00	-14.00
			CXE		-15.00	-15.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
570.000	525.000	4.84	DF	-25.00	-25.00	Surr-13C7-PFUnA
			CE		-16.00	-16.00
			CXE		-12.00	-12.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
615.000	570.000	5.15	DF	-25.00	-25.00	Surr-13C2-PFDoA
			CE		-18.00	-18.00
			CXE		-15.00	-15.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

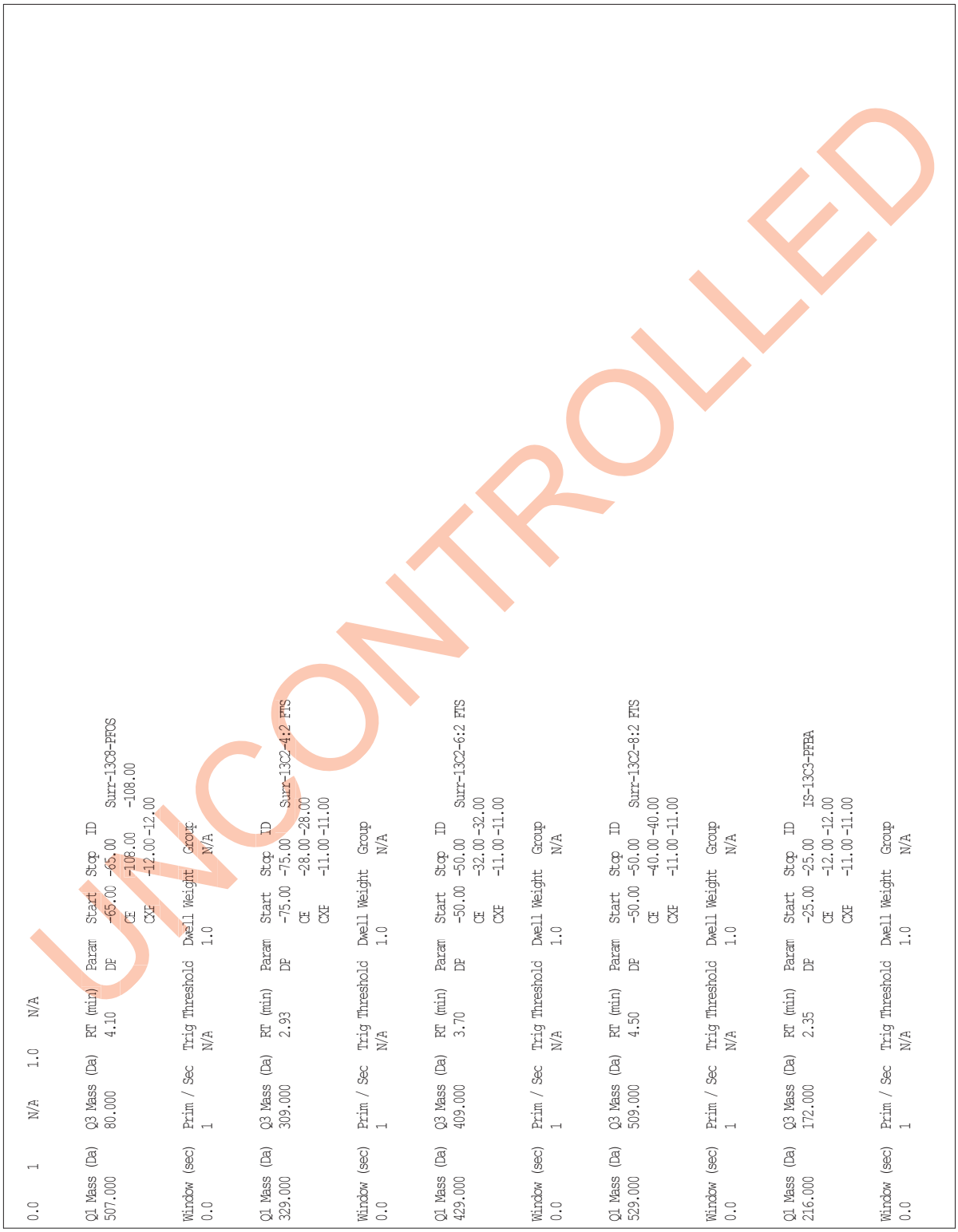
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
302.000	80.000	2.69	DF	-55.00	-55.00	Surr-13C3-PFBS
			CE		-58.00	-58.00
			CXE		-12.00	-12.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
402.000	80.000	3.35	DF	-60.00	-60.00	Surr-13C3-PFHxS
			CE		-74.00	-74.00
			CXE		-12.00	-12.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group

Attachment V: Instrument Conditions (cont'd)-p9



0.0 1 N/A 1.0 N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
507.000	80.000	4.10	DP	-65.00	-65.00	Surr-13C8-PFOS
			CE	-108.00	-108.00	
			CXP	-12.00	-12.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
329.000	309.000	2.93	DP	-75.00	-75.00	Surr-13C2-4:2 FTS
			CE	-28.00	-28.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
429.000	409.000	3.70	DP	-50.00	-50.00	Surr-13C2-6:2 FTS
			CE	-32.00	-32.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
529.000	509.000	4.50	DP	-50.00	-50.00	Surr-13C2-8:2 FTS
			CE	-40.00	-40.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

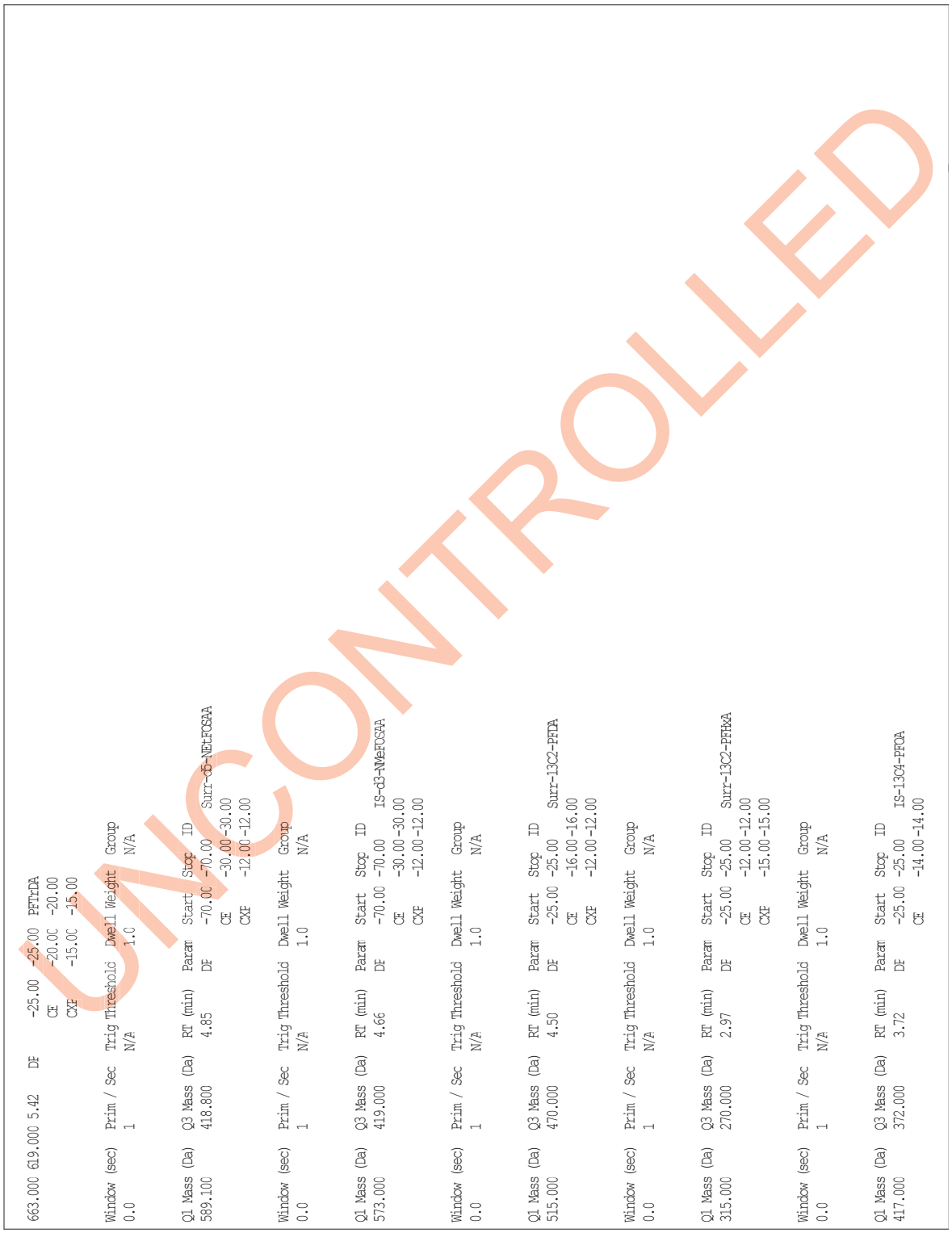
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Param	Start	Stop	ID
216.000	172.000	2.35	DP	-25.00	-25.00	IS-13C3-PFBA
			CE	-12.00	-12.00	
			CXP	-11.00	-11.00	

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

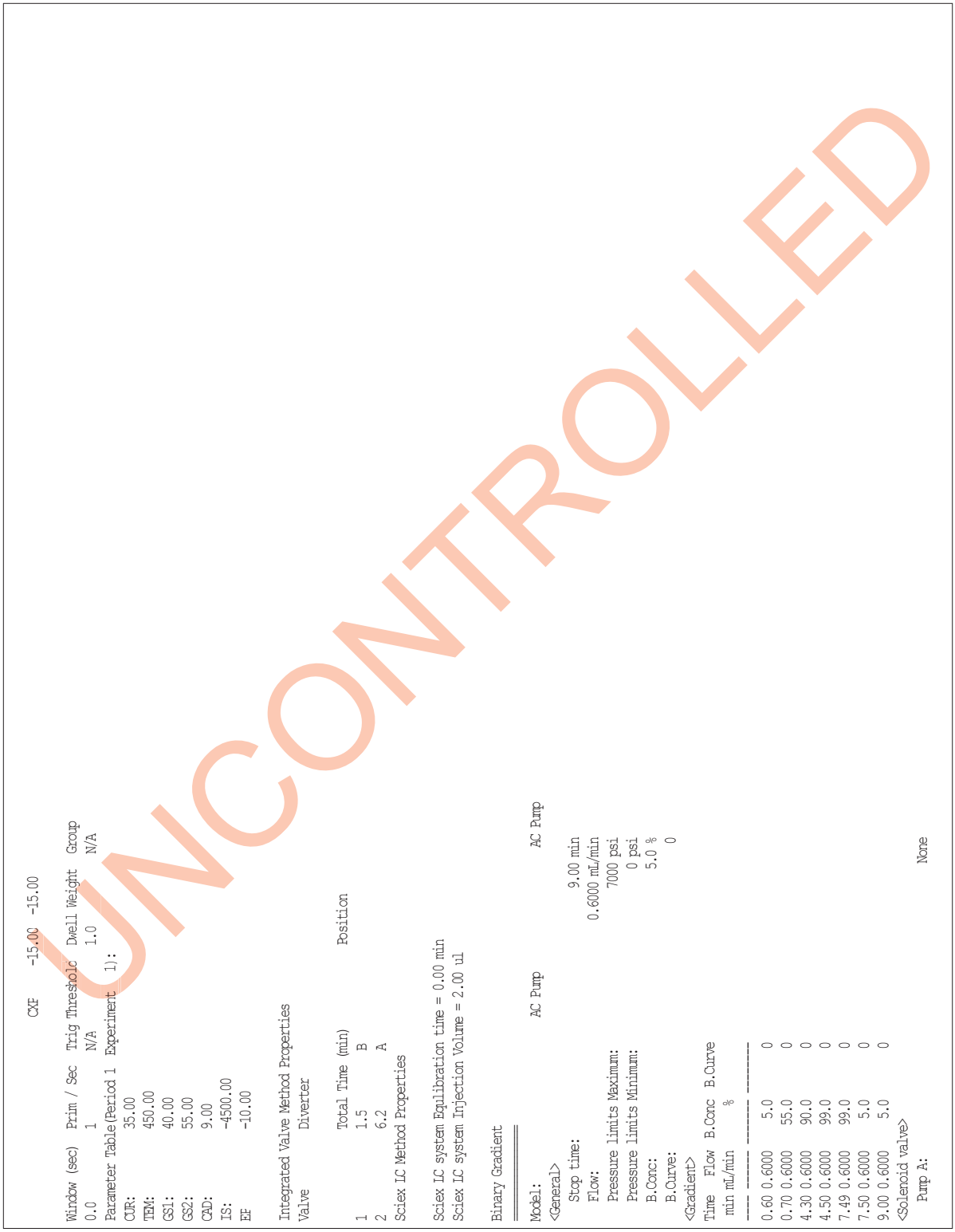
Attachment V: Instrument Conditions (cont'd)-p10

Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Parar	Start	Stop	ID
415.000	370.000	3.72	DP	-25.00	-25.00	IS-13C2-PFOA
			CE		-14.00	-14.00
			CXF		-11.00	-11.00
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight		Group	
0.0	1	N/A	1.0		N/A	
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Parar	Start	Stop	ID
503.000	80.000	4.10	DP	-65.00	-65.00	IS-13C4-PFOS
			CE		-108.00	-108.00
			CXF		-11.00	-11.00
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight		Group	
0.0	1	N/A	1.0		N/A	
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Parar	Start	Stop	ID
584.000	419.000	4.85	DP	-70.00	-70.00	N-EtFOSAA
			CE		-28.00	-28.00
			CXF		-12.00	-12.00
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight		Group	
75.0	1	N/A	1.0		N/A	
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Parar	Start	Stop	ID
570.000	419.000	4.66	DP	-70.00	-70.00	N-MeFOSAA
			CE		-30.00	-30.00
			CXF		-12.00	-12.00
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight		Group	
75.0	1	N/A	1.0		N/A	
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Parar	Start	Stop	ID
713.000	669.000	5.66	DP	-25.00	-25.00	PFTA
			CE		-22.00	-22.00
			CXF		-15.00	-15.00
Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight		Group	
0.0	1	N/A	1.0		N/A	
Q1 Mass (Da)	Q3 Mass (Da)	RT (min)	Parar	Start	Stop	ID

Attachment V: Instrument Conditions (cont'd)-p11



Attachment V: Instrument Conditions (cont'd)-p12



CXF -15.00 -15.00

Window (sec)	Prim / Sec	Trig Threshold	Dwell Weight	Group
0.0	1	N/A	1.0	N/A

Parameter Table(Period 1 Experiment 1):
CUR: 35.00
TEM: 450.00
GS1: 40.00
GS2: 55.00
CAD: 9.00
IS: -4500.00
EP -10.00

Integrated Valve Method Properties
Valve Diverter

	Total Time (min)	Position
1	1.5	B
2	6.2	A

Sciex LC Method Properties

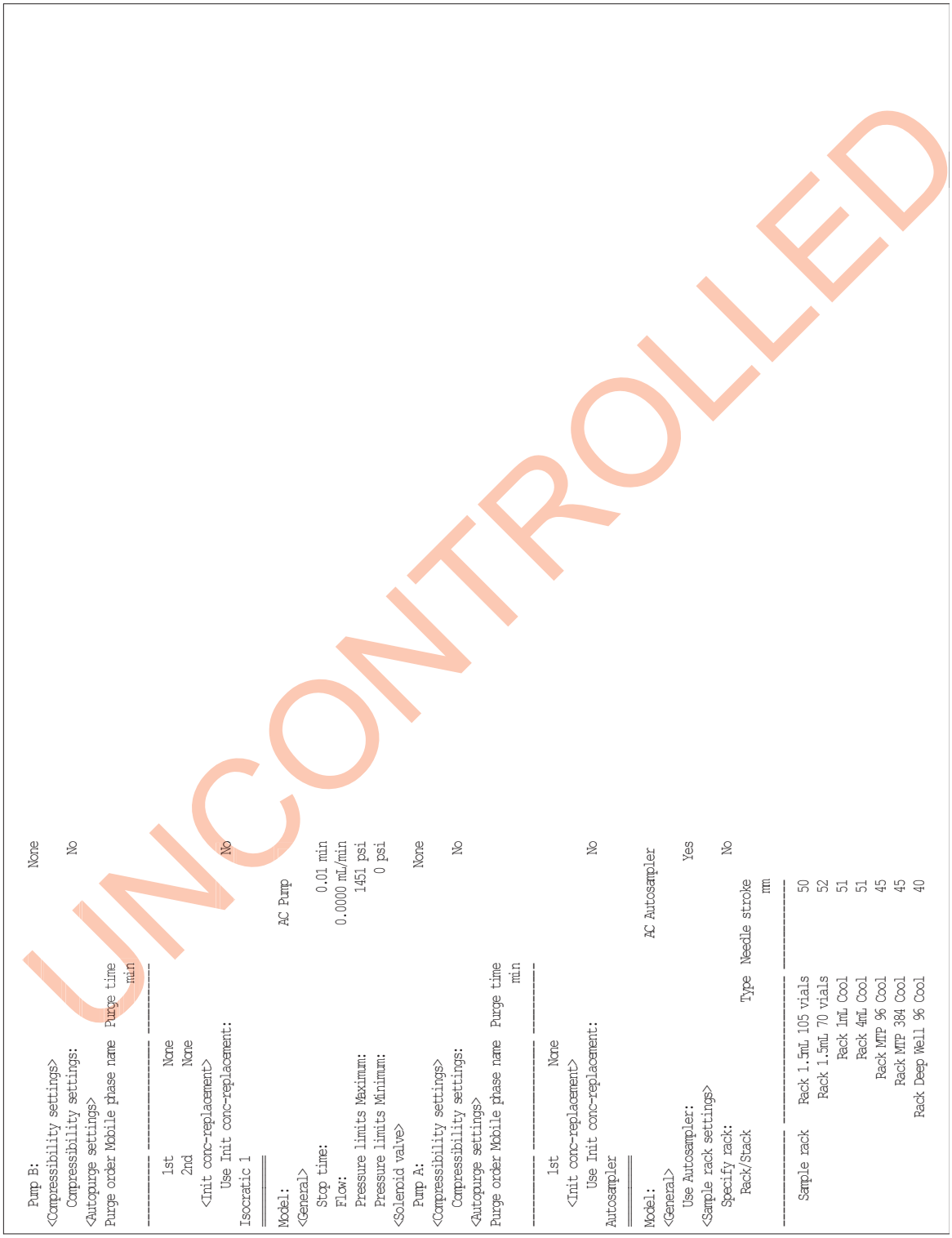
Sciex LC system Equilibration time = 0.00 min
Sciex LC system Injection Volume = 2.00 ul

Binary Gradient
Model: AC Pump
<General> AC Pump
Stop time: 9.00 min
Flow: 0.6000 mL/min
Pressure limits Maximum: 7000 psi
Pressure limits Minimum: 0 psi
B.Conc: 5.0 %
B.Curve: 0
<Gradient>

Time min	Flow mL/min	B.Conc %	B.Curve
0.60	0.6000	5.0	0
0.70	0.6000	55.0	0
4.30	0.6000	90.0	0
4.50	0.6000	99.0	0
7.49	0.6000	99.0	0
7.50	0.6000	5.0	0
9.00	0.6000	5.0	0

<Solenoid valve> None
Pump A:

Attachment V: Instrument Conditions (cont'd)-p13



Pump B: None
<Compressibility settings>
Compressibility settings: No
<Autopurge settings>

Purge order	Mobile phase name	Purge time min
1st	None	
2nd	None	

<Init conc-replacement>
Use Init conc-replacement: No
Isocratic 1

Model: AC Pump
<General>

Stop time:	0.01 min
Flow:	0.0000 mL/min
Pressure limits Maximum:	1451 psi
Pressure limits Minimum:	0 psi

<Solenoid valve>
Pump A: None
<Compressibility settings>
Compressibility settings: No
<Autopurge settings>

Purge order	Mobile phase name	Purge time min
1st	None	

<Init conc-replacement>
Use Init conc-replacement: No
Autosampler

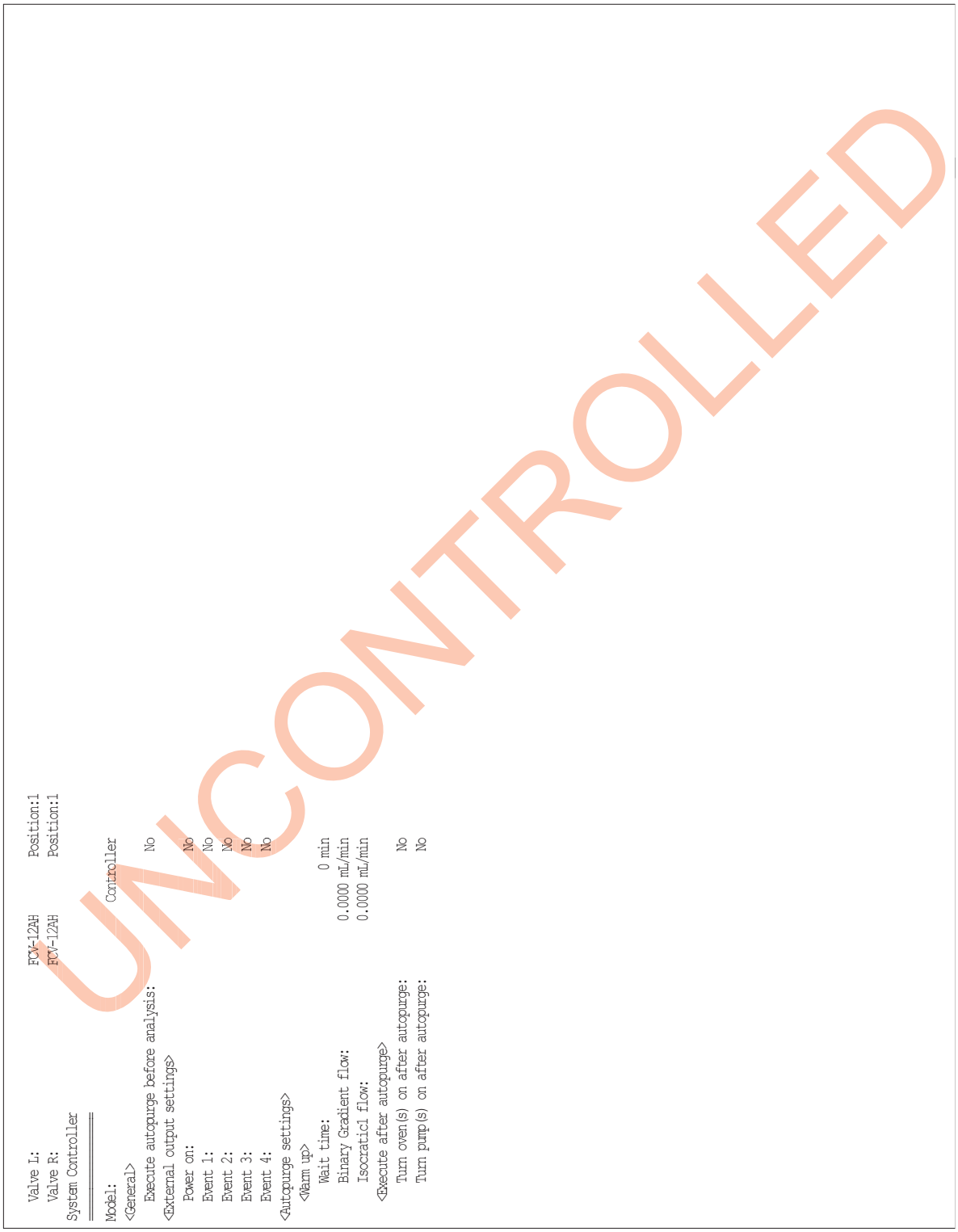
Model: AC Autosampler
<General>
Use Autosampler: Yes
<Sample rack settings>
Specify rack: No

Rack/Stack	Type	Needle stroke mm
Sample rack	Rack 1.5mL 105 vials	50
	Rack 1.5mL 70 vials	52
	Rack 1mL Cool	51
	Rack 4mL Cool	51
	Rack MTP 96 Cool	45
	Rack MTP 384 Cool	45
	Rack Deep Well 96 Cool	40

Attachment V: Instrument Conditions (cont'd)-p14

```
                 Rack Deep Well 384 Cool        40
Changer stack D                 MTP 96          45
                                DWP 96          45
                                 1.5mL          44
                                MTP 384         45
                                DWP 384         45
Changer stack C                 MTP 96          45
                                DWP 96          45
                                 1.5mL          44
                                MTP 384         45
                                DWP 384         45
Changer stack B                 MTP 96          45
                                DWP 96          45
                                 1.5mL          44
                                MTP 384         45
                                DWP 384         45
Changer stack A                 MTP 96          45
                                DWP 96          45
                                 1.5mL          44
                                MTP 384         45
                                DWP 384         45
<Injection settings>
  Sampling speed:                              5 µL/s
  Use cooler temperature:                         Yes
  Cooler temperature:                           15 °C
  Control vial needle stroke:                   50 mm
<Acquisition cycle time optimization>
  Pretreatment start timing:                      Off
<Rinse settings>
  Rinse mode:               Before and after aspiration
  Rinse dip time:                                 0 s
  Rinsing speed:                              35 µL/s
  Rinsing volume:                              500 µL
<Purge settings>
  Purge time:                                25.0 min
<Autopurge settings>
  Execute sampler purge:                           No
Column Oven
========
Model:                                 AC Column Oven
<General>
  Use Column Oven:                                Yes
  Oven temperature:                             40 °C
  Temperature limit(Maximum):                   90 °C
<Advanced>
  Wait for temperature equilibration before run:  Yes
<Valve>
```

Attachment V: Instrument Conditions (cont'd)-p15



```
   Valve L:                    FCV-12AH      Position:1
   Valve R:                    FCV-12AH      Position:1
System Controller
=================
Model:                         Controller
<General>
  Execute autopurge before analysis:                No
<External output settings>
  Power on:                                         No
  Event 1:                                          No
  Event 2:                                          No
  Event 3:                                          No
  Event 4:                                          No
<Autopurge settings>
  <Warm up>
    Wait time:                                      0 min
    Binary Gradient flow:                   0.0000 mL/min
    Isocratic1 flow:                        0.0000 mL/min
  <Execute after autopurge>
    Turn oven(s) on after autopurge:                  No
    Turn pump(s) on after autopurge:                  No
```

Attachment VI: Method QC Summary

QC TYPE	CONCENTRATION LEVEL	FREQUENCY	ACCEPTANCE CRITERIA
Analysis Batch		Begins and ends with the appropriate CCCs. Maximum of 20 extracted field samples.	
Extraction Batch		No more than 20 field samples by the same person during a work day using the same lots of supplies.	
Initial Calibration	A minimum of 5 (linear) calibration points , the lowest must be at or lower than the MRL. Minimum 6 points required for Quadratic regression	Run during initial method set up. Run appropriate CCCs for subsequent batches, if CCCs do not meet recovery criteria, run initial calibration	Back calculate the analyte concentration and recoveries must be within 50-150% for points at or below the MRL and within 70-130% for other points.
Continuing Calibration Check (CCC)	CCL (2.0 ng/L), CCM (30 ng/L), or CCH (50 ng/L).	A CCL must be analyzed immediately after the initial calibration curve, prior to any QC or samples. Rotate CCM and CCH after every tenth field sample and at the end of each analysis batch.	Recovery must be within 50-150% of the true value for CCL and within 70-130% for CCM and CCH.
Unextracted Mid-level QCS (QCS)	20 ng/L	Analyze as part of the IDC, at least quarterly, or with each new calibration prep.	Recovery must be within 70-130% of the true value.
Internal Standard	40 ng/L in terms of IS PFOA-$^{13}C_4$.	Introduce into every field sample, calibration, and QC sample.	IS area counts must be 50-150% of the average IS area count from the initial calibration and 70-140% of the most recent CCC
Surrogate	40 ng/L in terms of $^{13}C_2$-PFHxA	Introduce into every field sample, calibration, and QC sample.	Recovery must be within 70-130% of the target value.
Lab Reagent Blank (LRB/MBLK)	Reagent Water prepared, and analyzed as a sample.	Include one LRB/MBLK with each extraction batch.	Results must be less than 1/3 the MRL.

QC TYPE	CONCENTRATION LEVEL	FREQUENCY	ACCEPTANCE CRITERIA
		If an automated system is used, the LRBs should be rotated among the ports	
Lab Fortified Blank (LFB/LCS)	LFB-L (2.0 ng/L), LFB-M (25 ng/L), or LFB-H (50 ng/L).	LFB-L per day. As well as LFB-M or LFB-H rotated per batch	70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Lab Fortified Sample Matrix (LFSM/MS)	Rotate between low (2.0 ng/L), mid (25 ng/L), and high (50 ng/L) between extraction batches.	Include one LFSM/MS per extraction batch (20 samples or less).	70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Lab Fortified Sample Matrix Duplicate (LFSMD/MSD)/Field Duplicate (FD/DUP)	For LFSMD, rotate between low (2.0 ng/L), mid (30 ng/L), and high (30 ng/L) between extraction batches.	Include at least one FD/DUP or LFSMD/MSD with each extraction batch.	RPD must be less than or equal to 50% for analytes within 2x the MRL. RPDs less than or equal to 30% for analytes higher than 2x the MRL. For LFSMD, 70-130% recovery for mid- and high-levels. 50-150% recovery for low-level.
Field Reagent Blank (FRB)	Reagent Water prepared, and analyzed as a sample.	Process only if an associated field sample contains an analyte at or above the MRL.	Results must be less than or equal to 1/3 the MRL.
Initial Demonstration of Low System Background	Prepare, extract, and analyze as a sample.	Analyze an extracted LRB prior to any other IDC steps. If an automated system is used, the LRBs must be extracted from each port. After IDC, LRB should be rotated among the ports	Results must be less than 1/3 the MRL.
Initial Demonstration of Precision	Prepare, extract and analyze 7 replicate LFB/LCSs fortified at 25 ng/L.	When beginning the use of this method, with each new analyst, and after a major change in instrumentation.	RSD must be less than 20% for the analytes.

QC TYPE	CONCENTRATION LEVEL	FREQUENCY	ACCEPTANCE CRITERIA
Initial Demonstration of Accuracy	Use the same results obtained from the Initial Demonstration of Precision.	When beginning the use of this method, with each new analyst, and after a major change in instrumentation.	Mean recovery must be within 70-130%.
Continuing Demonstration of Capability		MDL and Precision and Accuracy performed annually for each analyst or extractionist.	RSD must be less than 20% for the analytes. Mean recovery must be within 70-130%.
MRL Confirmation	Prepare, extract and analyze 7 replicate LFB/LCSs fortified at the proposed MRL.	Initially on each instrument and whenever there is a major change in instrumentation. Each new analyst and extractionist, performing this method.	The upper PIR limits must be less than or equal to 150%. The lower PIR limits must be greater than or equal to 50%.
LFB/LFBDup (LCS/LCSDup)	Rotate between mid (25 ng/L), and high (50 ng/L) between extraction batches.	For Arizona samples when MS/MSD failed acceptance for accuracy and precision	RPDs less than or equal to 30%. 70-130% recovery.
Establish RT for both linear and branched isomers	Run at mid to high level concentration	Run as part of IDC Repeat anytime chromatographic changes occur that alter analyte retention time.	All isomers of each analyte must elute with the same MRM window

Attachment VII: Analytical Sequence

Cal Std1

Cal Std2

Cal Std3

Cal Std4

Cal Std5 - Peak Assymetry Factor calculation

Cal Std6

CCC at MRL Level

QCS at Mid-level

LRB/MBLK

LFB at MRL level

LFB

FS (Field Sample) 1

LFSM/MS on FS 1

LFSMD/MSD on FS 1

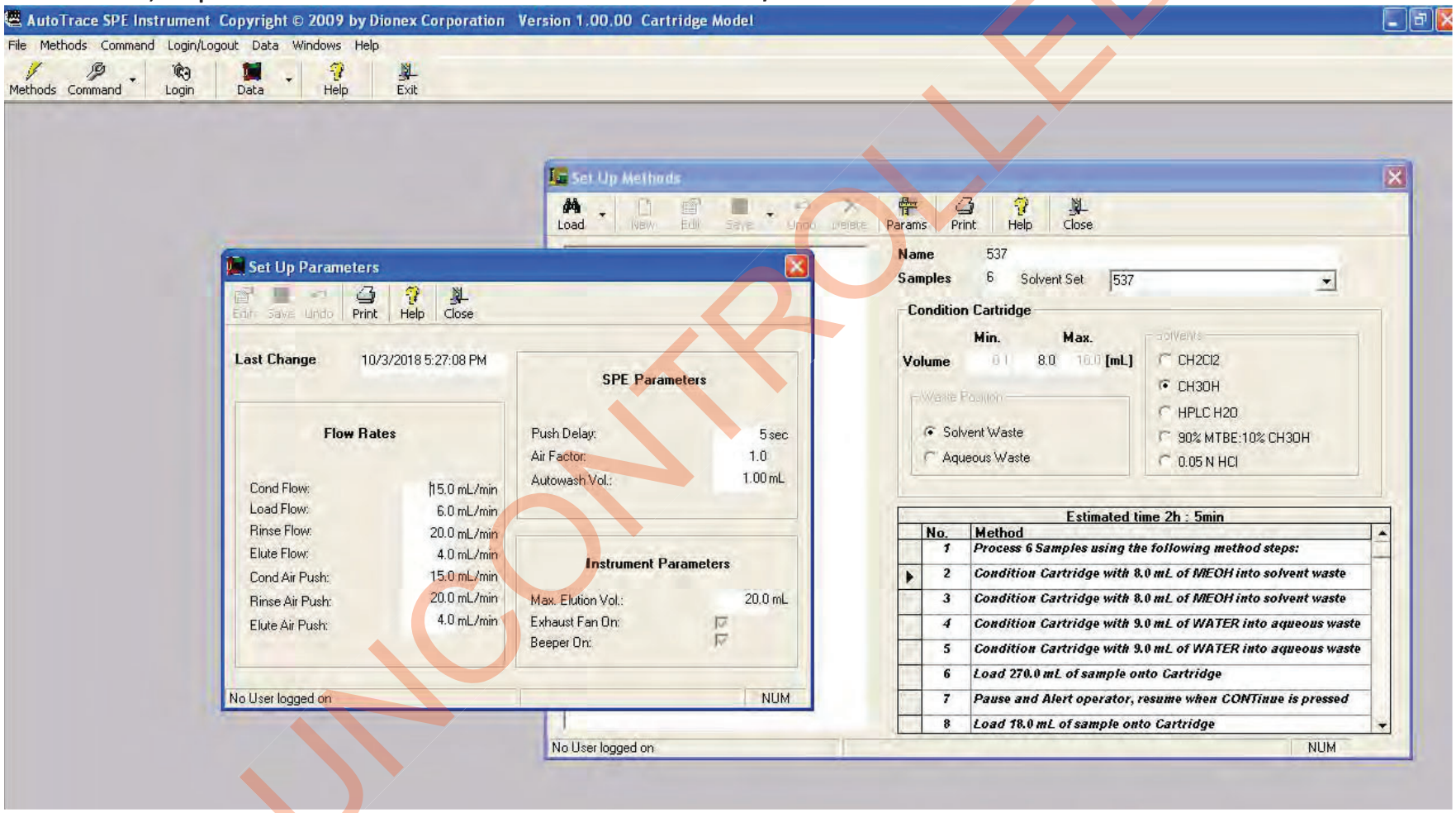
FS 2 to FS 10

Mid-level CCC

FS 11 to FS 20

High-level CCC

Attachment IX, Caliper Lifesciences Automated SPE Workstation Conditions/Parameters



Attachment X Procedure for pH and Free Chlorine Checks

Note: The pH must be verified prior to checking for free chlorine. See Extractions-WI23106, pH and Chlorine Check for Extractions

1. pH Verification
   a) Check the initial pH of the sample and record it on the backlog, which will later be entered in ~~the webform sheet~~TALS. The pH must be between 6.5 and 7.5.
   b) If the sample pH is out of range, verify the pH of the back-up container.
   c) If the the pH of the back-up container is also out of range, notify the ASM and supervisor of the non-compliant sample.
   d) If allowed by the client, add approximately 1.25 g of trizma to the sample bottle. Verify the final pH and record it on the backlog.
   e) If the final pH is within range, extract the sample and generate a QIR. If the final pH is not within range, do not add more trizma. Extract the sample and generate a QIR, while noting that the pH requirement was not met.

2. Free Chlorine Check
   a) Check and record the initial free chlorine using the DPD free chlorine reagent and approximately 10 mL of sample. Free chlorine must be less than 0.1 ppm.
   b) If the color of the sample turns pink after addition of the reagent, verify the presence of chlorine using the SenSafe strips.
   c) If free chlorine is verified, check the back-up container for free chlorine.
   d) If the back-up container also fails, notify the ASM and supervisor of the non-compliant sample.
   e) If allowed by the client, add approximately 1.25 g of trizma to the sample bottle. Check and record the final free chlorine.
   f) If free chlorine is less than 0.1 ppm, extract the sample and generate a QIR. If free chlorine is still present, notify the ASM and request that the client re-sample

Note: Excessive amounts of trizma may result in low surrogate recovery

Attachment XI EPA email with regards to Trizma preservation

Dean, Robert

To: Ramos, Marnellie
Subject: RE: EPA 537.1 - re ph andresidual chlorine from Jody Shoemaker

From: Ali Haghani
Sent: Monday, April 15, 2019 8:10 AM
To: Nilda Cox
Subject: FW: EPA 537

Response to EPA 537 preservation

From: Shoemaker, Jody [mailto:shoemaker.jody@epa.gov]
Sent: Monday, April 15, 2019 4:53 AM
To: Ali Haghani
Subject: RE: EPA 537

EXTERNAL EMAIL*

Ali,

Trizma only sequesters free chlorine and reduces it to the weaker oxidant, chloramine. Thus, when measuring free chlorine, it has to be measured very quickly or the chloramine will cause color to form with time.

I know this came up during UCMR 3 so I will ask OGWDW what their guidance was to labs since I don't remember now.

As for adding Trizma at the bench – have you actually determined that the samples in questions are not buffered near pH 7? Just because they have chloramine present doesn't mean they are not buffered.

You should not have a need to add more Trizma to drinking water samples to meet the pH requirements of the method.

Regarding M559-Dan's plan is to finish the edits of the draft method today and send it out by the end of the day. Sorry, but we were both off work on Friday so did not get your email until this morning. Thank you for your willingness to participate in this verification.

Sincerely,
Jody

Dr. Jody Shoemaker
EPA/National Exposure Research Laboratory
26 W. Martin Luther King Drive
MS 587
Cincinnati, OH 45268
513-569-7298 (office)
shoemaker.jody@epa.gov

From: Ali Haghani <AliHaghani@eurofinsUS.com>
Sent: Thursday, April 11, 2019 10:51 PM
To: Shoemaker, Jody <shoemaker.jody@epa.gov>
Subject: EPA 537

Hello Jody;
I am looking forward again to do collaboration for your new method EPA 559 and in order to start preparing for it can I please have a copy of it right now - if possible so that I can go over it over the weekend.
Also I know EPA 537 adds Trizma for making all samples the same pH for extraction reproducibility. However, probably due to a policy or something outside the method itself chlorine check needs to be performed.
My question is that we occasionally receive samples that have still hits for chlorine is it possible to add additional Trizma at the bench to neutralize prior to extraction to omit resampling? My current understanding is that chlorine does not have adverse effect on the targeted compounds.
In addition we have found that DPD chlorine check can have false positives and we use strips to make sure samples are free of dissolved chlorine.

Kindest regards
Ali

Notify us here to report this email as spam.

* WARNING - EXTERNAL: This email originated from outside of Eurofins. Do not click any links or open any attachments unless you trust the sender and know that the content is safe!

Attachment XII EPA email with regards to Field Blanks

Dean, Robert

To: Cox, Nilda; Ramos, Marnellie; Rodriguez, Eduardo
Subject: RE: 537.1 Rev 2 Clarifications from Jody

From: Shoemaker, Jody [mailto:shoemaker.jody@epa.gov]
Sent: Thursday, August 27, 2020 12:32 PM
To: Nilda Cox <NildaCox@eurofinsUS.com>
Subject: RE: 537.1 Rev 2 Clarifications

EXTERNAL EMAIL*

Nilda,
The changes to the FRB were made in order for M537.1 to be consistent with Method 533 which was published after the first version of Method 537.1 came out. There really isn't much scientific difference but we decided we thought it would make it less confusing if M537.1 and M533's FRB were prepared in the same manner.

Hopefully this makes things clearer.

Jody

Dr. Jody Shoemaker
EPA/Center for Environmental Solutions and Emergency Response
26 W. Martin Luther King Drive
MS 689
Cincinnati, OH 45268
513-569-7298 (office)
shoemaker.jody@epa.gov

From: Nilda Cox <NildaCox@eurofinsUS.com>
Sent: Thursday, August 27, 2020 3:01 PM
To: Shoemaker, Jody <shoemaker.jody@epa.gov>
Subject: 537.1 Rev 2 Clarifications

Again – I need your assistance on 537.1 rev 2 . thank you for your previous assistance.
1. Need to clarify section 8.3 .1 changes . Please see below for my comments in blue highlights
2. I think the first paragraph was changed but the second paragraph was left alone coming from the original 537.1 revision 1)
3. Also – 537.1 rev 2 - stated that updates were editorial changes . Is section 8.3.1 changes intended to be editorial changes only ? thank you

8.3. FIELD REAGENT BLANKS (FRB)
8.3.1.
An FRB must be handled along with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. At the laboratory, fill the field blank sample bottle with reagent water, then seal, and ship to the sampling site along with the sample bottles.
(1.Nilda - so the reagent water is not preserved)

For each FRB shipped, a second FRB bottle containing only the preservative must also be shipped. (2.Nilda - The FRB bottle now has preservative).

At the sampling site, the sampler must open the shipped FRB and pour the preserved reagent water (3Nilda -this one is preserved reagent water – inconsistent on the above item 1)
into the empty shipped sample bottle, (4. Nilda – this is empty - inconsistent with item 2) seal and label this bottle as the FRB.
The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAS were not introduced into the sample during sample collection/handling.

thank you for your assistance .
regards

Nilda Cox
Quality Assurance Manager/Regulatory Consulting Manager

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Please note: In order to continue to provide critical testing services, **Eurofins Environment Testing laboratories in the US are maintaining our courier services and continue to sample, analyze and report all test data as usual.** The situation around COVID-19 continues to be fluid and we are continuing to follow local and government mandates as applicable. For up-to-date business information, visit our website and follow us on Facebook and LinkedIn.

Links to use:

Website: https://www.eurofinsus.com/environment-testing
Facebook: https://www.facebook.com/EurofinsEnvTesting
LinkedIn: https://www.linkedin.com/company/eurofins-env-testing-america

United States Environmental Protection Agency

Office of Water

www.epa.gov August 2021

Draft Method 1633

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

U.S. Environmental Protection Agency
Office of Water (4303T)
Office of Science and Technology
Engineering and Analysis Division
1200 Pennsylvania Avenue, NW
Washington, DC 20460

EPA 821-D-21-001

Draft Method 1633
Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

August 2021

Notice

This document re resents a draft of a P AS method currently under develo ment by the EPA Office of Water, Engineering and Analysis Division (EAD), in conjunction ith the De artment of Defense (DOD). **This method is not required for Clean Water Act compliance monitoring until it has been proposed and promulgated through rulemaking.**

A single-laboratory validation of the rocedure has been com leted and the re ort on the results of that study is being re ared. istorically, EAD osts draft methods on the Clean Water Act ebsite after the single-laboratory validation re ort is com leted. o ever, due to a large number of ublic and sta eholder re uests, this method is being osted on the eb before the single-laboratory validation study re ort is finali ed. A revision of this draft method ith a later ublication date may be issued at that time. No rocedural changes are e ected as a result of the single-laboratory validation, but some of the erformance data (hich are resented only as e am les) may change once the statistical analysis of the single-laboratory validation data is com leted.

This draft method has been subjected to multi le levels of revie across several EPA Program Offices. DOD e ects to begin a multi-laboratory validation study of the rocedure in late 2021, in collaboration ith the Office of Water and the Office of and and Emergency Management.

The Office of Water ill use the results of the multi-laboratory validation study to finali e the method and add formal erformance criteria. The method validation rocess may eliminate some of the arameters listed in this draft method.

n the meantime, the Office of Water is releasing this draft on its eb site. aboratories, regulatory authorities, and other interested arties are encouraged to revie the method, and here a ro riate, utili e it for their o n ur oses, ith the e licit understanding that this is a draft method, subject to revision.

Acknowledgements

This draft method as re ared under the direction of Adrian anley of the Engineering and Analysis Division, Office of Science and Technology, ithin EPA s Office of Water, in collaboration ith the De artment of Defense.

EPA ac no ledges the su ort of a number of organi ations in the develo ment and validation of this draft method, including the develo ers of the original rocedure, the De artment of Defense, the members of EPA s or grou , and EPA s su ort contractor staff at eneral Dynamics nformation Technology, including

Adrian anley	EPA Office of Water, Office of Science and Technology, Engineering and Analysis Division
S. e ah ur et	EPA Office of Water, Office of Science and Technology, Engineering and Analysis Division
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Coreen amilton	S S-A S Analytical
vona ys	S S-A S Analytical
Ting Chen	S S-A S Analytical
enry uang	S S-A S Analytical
Mirna Al i ar	eneral Dynamics nformation Technology
arrry McCarty	eneral Dynamics nformation Technology

Disclaimer

See the notice on the title age regarding the status of this method.

Mention of trade names or commercial roducts does not constitute endorsement or recommendation for use.

Contact

Please address uestions, comments, or suggestions to

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htt s .e a.gov c a-methods forms contact-us-about-c a-analytical-methods

Table of Contents

DRAFT Method 1633 - Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

1.0 Scope and Application

1.1 Method 1633 is for use in the Clean Water Act (CWA) for the determination of the per- and polyfluoroalkyl substances (PFAS) in Table 1 in aqueous, solid (soil, biosolids, sediment) and tissue samples by liquid chromatography/mass spectrometry (LC-MS/MS).

1.2 The method calibrates and quantifies PFAS analytes using isotopically labeled standards. Where linear and branched isomers are present in the sample and either qualitative or quantitative standards containing branched and linear isomers are commercially available, the PFAS analyte is reported as a single analyte consisting of the sum of the linear and branched isomer concentrations.

1.3 The instrumental portion of this method is for use only by analysts experienced with LC-MS/MS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.4 By their very nature, many components of PFAS present analytical challenges unique to this class of analytes. For example, PFAS analytes readily adhere to the walls of the sample containers and may also stratify in the container. EPA has included procedures in the method that must be employed to address such challenges (see Section 11.0 and Appendices A and B).

1.5 This method is "performance-based," which means that modifications may be made without additional EPA review to improve performance (e.g., overcome interferences, or improve the sensitivity, accuracy, or precision of the results) *provided that* all performance criteria in this method are met. Requirements for establishing equivalency are in Section 9.1.2 and include 9.1.2.2c. For CWA uses, additional flexibility is described at 40 CFR 136.6. Changes in performance, sensitivity, selectivity, precision, recovery, etc., that result from modifications within the scope of 40 CFR Part 136.6, and Section 9.0 of this method must be documented, as well as how these modifications compare to the specifications in this method. Changes outside the scope of 40 CFR Part 136.6 and Section 9.0 of this method may require prior review or approval.

2.0 Summary of Method

Environmental samples are prepared and extracted using method-specific procedures. Sample extracts are subjected to cleanup procedures designed to remove interferences. Analyses of the sample extracts are conducted by LC-MS/MS in the multiple reaction monitoring (MRM) mode. Sample concentrations are determined by isotope dilution or extracted internal standard quantification (see Section 10.3) using isotopically labeled compounds added to the samples before extraction.

2.1 Extraction

2.1.1 Aqueous samples are spiked with isotopically labeled standards, extracted using solid-phase extraction (SPE) cartridges and undergo cleanup using carbon before analysis.

2.1.2 Solid samples are spiked with isotopically labeled standards, extracted into basic methanol, and cleaned up by carbon and SPE cartridges before analysis.

2.1.3 Tissue sam les are s i ed ith isoto ically labeled standards, e tracted in otassium hydro ide and acetonitrile follo ed by basic methanol, and cleaned u by carbon and SPE cartridges before analysis.

2.2 This method measures the analytes as either their anions or neutral forms. The default a roach for Clean Water Act uses of the method is to re ort the analytes in their acid or neutral forms, using the e uations in Section 1 .2, although the differences bet een the anion and acid form concentrations are minimal (See Table 8). Other roject-s ecific re orting schemes may be used here re uired.

2.3 ndividual P AS analytes are identified through ea analysis of the uantification and confirmation ions, here a licable.

2.4 uantitative determination of target analyte concentrations is made ith res ect to an isoto ically labeled P AS standard the concentrations are then used to convert ra ea areas in sam le chromatograms to final concentrations.

2.5 esults for target analytes are recovery corrected by the method of uantification (i.e., either isoto e dilution or e tracted internal standard uantification, see Section 10.3). soto ically labeled com ound recoveries are determined by com arison to the res onses of one of seven non-e tracted internal standards (a. .a., the recovery standards) and are used as general indicators of overall analytical uality.

2.6 The uality of the analysis is assured through re roducible calibration and testing of the e traction, cleanu , and C-MS MS systems.

3.0 Definitions

Definitions are rovided in the glossary at the end of this method.

4.0 Contamination and interferences

4.1 Solvents, reagents, glass are, and other sam le rocessing hard are may yield artifacts and elevated baselines causing misinter retation of chromatograms. S ecific selection of reagents and solvents may be re uired.

4.2 Clean all e ui ment rior to, and after each use to avoid P AS cross-contamination. Ty ical cleaning solvents used include ater, methanol, and methanolic ammonium hydro ide. The residual P AS content of dis osable lastic are and filters must be verified by batch lot number and may be used ithout cleaning if P AS levels are less than half the Minimum evel (M , see Table 6).

4.2.1 All glass e ui ment that is used in the re aration or storage of reagents is cleaned by ashing ith detergent and ba ing in a iln or furnace (Section 6.2.2). After detergent ashing, glass are should be rinsed immediately ith reagent ater. Prior to use, ba ed glass are must be solvent rinsed and then air dried. A solvent rinse rocedure using methanolic ammonium hydro ide (1), toluene, and methanol is recommended.

4.2.2 All arts of the SPE manifold must be cleaned bet een sam les by sonicating in methanolic ammonium hydro ide (1) and air drying rior to use. Smaller arts, li e the needles, ada ters, reservoirs, and sto coc s associated ith the manifold re uire rinsing

ith ta ater rior to sonicating in methanolic ammonium hydro ide (1) and air drying. When in use, after loading the sam les but rior to elution rocedures, the chamber must be rinsed ith methanolic ammonium hydro ide (1).

4.2.3 All e ui ment used in the filleting, dissecting, shuc ing, com ositing, and homogeni ation of tissue must be cleaned ith detergent and hot ater, then rinsed ith ultra- ure ater follo ed by a series of solvent rinses. A ty ical solvent rinse rocedure ould be acetone, follo ed by toluene, and then dichloromethane.

4.3 All materials used in the analysis must be demonstrated to be free from interferences by running method blan s (Section .) at the beginning and ith each sam le batch (sam les started through the e traction rocess on a given analytical batch to a ma imum of 20 field sam les).

4.3.1 The reference matri must simulate, as closely as ossible, the sam le matri being tested. deally, the reference matri should not contain P AS in detectable amounts but should contain otential interferents in the concentrations e ected to be found in the sam les to be analy ed.

4.3.2 or tissue, chic en breast or other similar animal tissue (see Section .2.3) may be used as the reference matri . The laboratory must verify that the source roduct used does not contain P AS in detectable amounts.

4.3.3 When a reference matri that simulates the sam le matri under test is not available, reagent ater (Section .2.1) can be used to simulate ater sam les and Otta a sand and or reagent-grade sand (Section .2.2) can be used to simulate soils.

4.4 nterferences co-e tracted from sam les ill vary considerably from source to source, de ending on the diversity of the site being sam led. nterfering com ounds may be resent at concentrations several orders of magnitude higher than the native P AS. ecause lo levels of P AS are measured by this method, elimination of interferences is essential. The cleanu ste s given in Section 12.0 can be used to reduce or eliminate these interferences and thereby ermit reliable determination of the P AS at the levels sho n in Table 6. The most fre uently encountered interferences are fluoro olymers ho ever, hen analy ing hole fish sam les, bile salts (e.g., Taurodeo ycholic Acid TDCA) can interfere in the chromatogra hy. or this reason, analysis of a standard containing TDCA is re uired as art of establishing the initial chromatogra hic conditions (see Sections 10.2.2. and 10.3.).

4.5 Each iece of reusable glass are may be numbered to associate that glass are ith the rocessing of a articular sam le. This may assist the laboratory in trac ing ossible sources of contamination for individual sam les, identifying glass are associated ith highly contaminated sam les that may re uire e tra cleaning, and determining hen glass are should be discarded.

5.0 Safety

5.1 The to icity or carcinogenicity of each chemical used in this method has not been recisely determined ho ever, each com ound should be treated as a otential health ha ard. E osure to these com ounds should be reduced to the lo est ossible level.

5.1.1 P OA has been described as li ely to be carcinogenic to humans. Pure standards should be handled by trained ersonnel, ith suitable rotection to s in and eyes, and care should be ta en not to breathe the va ors or ingest the materials.

5.1.2 t is recommended that the laboratory urchase dilute standard solutions of the analytes in this method. o ever, if rimary solutions are re ared, they must be re ared in a hood, follo ing universal safety measures.

5.2 The laboratory is res onsible for maintaining a current a areness file of Occu ational Safety and ealth Administration (OS A) regulations regarding the safe handling of the chemicals s ecified in this method. A reference file of safety data sheets (SDS) should also be made available to all ersonnel involved in these analyses. t is also suggested that the laboratory erform ersonal hygiene monitoring of each analyst ho uses this method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in eferences 1-4. The references and bibliogra hy at the end of eference 3 are articularly com rehensive in dealing ith the general subject of laboratory safety.

5.3 Sam les sus ected to contain these com ounds are handled using essentially the same techni ues em loyed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are re uired. Assistance in evaluating the health ha ards of articular laboratory conditions may be obtained from certain consulting laboratories and from State De artments of ealth or abor, many of hich have an industrial health service. Each laboratory must develo a strict safety rogram for handling these com ounds.

5.3.1 acility When finely divided sam les (dusts, soils, dry chemicals) are handled, all o erations (including removal of sam les from sam le containers, eighing, transferring, and mi ing) should be erformed in a glove bo demonstrated to be lea tight or in a fume hood demonstrated to have ade uate air flo . ross losses to the laboratory ventilation system must not be allo ed. andling of the dilute solutions normally used in analytical and animal or resents no inhalation ha ards e ce t in the case of an accident.

5.3.2 Protective e ui ment Dis osable lastic gloves, a ron or lab coat, safety glasses or mas , and a glove bo or fume hood ade uate for radioactive or should be used. During analytical o erations that may give rise to aerosols or dusts, ersonnel should ear res irators e ui ed ith activated carbon filters. Eye rotection (referably full-face shields) must be orn hile or ing ith e osed sam les or ure analytical standards. ate gloves are commonly used to reduce e osure of the hands.

5.3.3 Training Wor ers must be trained in the ro er method of removing contaminated gloves and clothing ithout contacting the e terior surfaces.

5.3.4 Personal hygiene ands and forearms should be ashed thoroughly after each mani ulation and before brea s (coffee, lunch, and shift).

5.3.5 Confinement solated or areas osted ith signs, segregated glass are and tools, and lastic absorbent a er on bench to s ill aid in confining contamination.

5.3.6 Waste andling ood techni ue includes minimi ing contaminated aste. Plastic bag liners should be used in aste cans. anitors and other ersonnel should be trained in the safe handling of aste.

5.3.7 aundry Clothing no n to be contaminated should be collected in lastic bags. Persons that convey the bags and launder the clothing should be advised of the ha ard and trained in ro er handling. The clothing may be ut into a asher ithout contact if the launderer no s of the otential roblem. The asher should be run through a cycle before being used again for other clothing.

5.4 iosolids sam les may contain high concentrations of bioha ards and must be handled ith gloves and o ened in a fume hood or biological safety cabinet to revent e osure. aboratory staff should no and observe the safety rocedures re uired in a microbiology laboratory that handles athogenic organisms hen handling biosolids sam les.

6.0 Equipment and Supplies

Note: *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the laboratory.*

6.1 Sam ling e ui ment for discrete or com osite sam ling

6.1.1 Sam le bottles and ca s

Note: *Do not use PTFE-lined caps on sample containers.*

6.1.1.1 i uid sam les (aters, sludges, and similar materials containing 0 mg solids er sam le) Sam le bottle, DPE, ith linerless DPE or oly ro ylene ca s.

Note: *At least two aliquots of aqueous samples are collected to allow sufficient volume for the determination of percent solids and for pre-screening analysis. One aliquot should be collected in a 500-mL container while the second aliquot may be collected in a smaller sample container (e.g., 250-mL or 125-mL).*

6.1.1.2 Solid sam les (soils, sediments, and biosolids that contain more than 0 mg solids) Sam le bottle or jar, ide-mouth, DPE, 00-m , ith linerless DPE or oly ro ylene ca s.

6.1.1.3 Tissue sam les Sam le jar, ide-mouth DPE, 100-m , ith linerless DPE or oly ro ylene ca s.

6.1.2 Com ositing e ui ment Automatic or manual com ositing system incor orating containers cleaned er bottle cleaning rocedure above. Only DPE tubing must be used. f the sam ler uses a eristaltic um , a minimum length of com ressible silicone rubber tubing may be used in the um only. efore use, the tubing must be thoroughly rinsed ith methanol, follo ed by re eated rinsing ith reagent ater to minimi e sam le contamination. An integrating flo meter is used to collect ro ortional com osite sam les.

6.2 E ui ment for glass are cleaning

Note: *If blanks from bottles or other glassware, show no detectable PFAS contamination when using fewer cleaning steps than required above, unnecessary cleaning steps and equipment may be eliminated.*

6.2.1 aboratory sin ith overhead fume hood

6.2.2 iln Ca able of reaching 4 0 C ithin 2 hours and maintaining 4 0 - 00 C 10 C, ith tem erature controller and safety s itch (Cress Manufacturing Co., Santa e S rings, CA, 31 , 31TS, or e uivalent). or safety, the iln or furnace should be vented outside the laboratory, or to a tra ing system.

6.3 E ui ment for sam le re aration

6.3.1 Polyethylene gloves

6.3.2 aboratory fume hood (of sufficient si e to contain the sam le re aration e ui ment listed belo)

6.3.3 love bo (o tional)

6.3.4 Tissue homogeni er Pro Scientific P O400DS homogeni er or e uivalent ith stainless steel macro-shaft and turbo-shear blade

6.3.5 Meat grinder obart, or e uivalent, ith 3- to -mm holes in inner late

6.3.6 E ui ment for determining ercent moisture

6.3.6.1 Oven Ca able of maintaining a tem erature of 110 C

6.3.6.2 Desiccator

6.3.7 alances

6.3.7.1 Analytical Ca able of eighing 0.1 mg

6.3.7.2 To loading Ca able of eighing 10 mg

6.3.8 Aluminum foil

6.3.9 Dis osable s oons, 10 mg, oly ro ylene or stainless steel

6.3.10 Ultrasonic mi er (sonicator)

6.3.11 DPE bottles, ith linerless DPE or oly ro ylene ca s 60 m

6.3.12 Pa er, range 0-14 - (Whatman Pan eha™ or e uivalent), 0. -unit readability

6.3.13 Analog or digital vorte mi er, single or multi-tube (isher Scientific 02-21 -4 2, or e uivalent)

6.3.14 olumetric flas s, Class A

6.3.15 Dis osable oly ro ylene collection tubes (13 100 mm, 8 m)

6.3.16 ariable s eed mi ing table (isherbrand™ Nutating mi er or e uivalent)

6.4 iltration

6.4.1 Silani ed glass ool (Sigma-Aldrich, Cat 20411 or e uivalent) store in a clean glass jar and rinsed ith methanol (2 times) rior to use.

6.4.2 Dis osable syringe filter, 2 -mm, 0.2- m Nylon membrane, PA Acrodisc or e uivalent

6.4.3 lass fiber filter, 4 mm, 1 m, PA A E or e uivalent

6.5 Centrifuge a aratus

6.5.1 Centrifuge (Thermo Scientific egend T , 16 cm rotor, or e uivalent), ca able of reaching at least 3000 r m

6.5.2 Centrifuge tubes Dis osable oly ro ylene centrifuge tubes (0 m)

6.6 Pi ettes

6.6.1 Norm- ect syringe (or e uivalent), oly ro ylene DPE, m

6.6.2 ariable volume i ettes ith dis osable DPE or oly ro ylene ti s (10 to m) used for re aration of calibration standards and s i ed sam les.

6.6.3 **Disposable** glass i ets

6.6.4 **Calibrated** mechanical i ettes or amilton graduated syringes

6.7 Solid-Phase E traction

6.7.1 Solid- hase e traction (SPE) cartridges (Waters Oasis WA 1 0 mg, Cat 1860024 3 or e uivalent). The SPE sorbent must have a a above 8 so that it remains ositively charged during the e traction.

Note: SPE cartridges with different bed volume (e.g., 500 mg) may be used; however, the laboratory must demonstrate that the bed volume does not negatively affect analyte absorption and elution, by performing the initial demonstration of capability analyses described in Section 9.2.

6.7.2 acuum manifold for SPE Cartridges (Waters™ e traction manifold WAT20060 or e uivalent)

6.8 Eva oration

6.8.1 Automatic or manual solvent eva oration system (Turbo a or e uivalent)

6.8.2 Eva oration concentrator tubes 60 m clear glass vial, 30 12 mm, ithout ca s (Wheaton Cat W226060 or e uivalent). Cover ith foil if re uired.

6.9 ials

6.9.1 Sna ca crim to vials, 300 , oly ro ylene (12 32 mm) used in sam le re-screening (DW ife Sciences Cat 22 180 or e uivalent)

6.9.2 Poly ro ylene crim sna vials, 1 m (Agilent Cat 182-0 6 or e uivalent)

6.9.3 Clear sna ca , P DC film hite silicone, 11 mm (American Chromatogra hy Su lies Cat C2 -11 or e uivalent)

6.9.4 Single ste filter vials (este Thomson S N E StEP Standard ilter ials, 0.2 µm Nylon membrane, with lac Preslit ca s Cat 2 8 1 or e uivalent) used in sam le re-screening.

6.10 nstrument

6.10.1 Ultra high- erformance li uid chromatogra h (UP C also called U P C) or high-erformance li uid chromatogra h (P C) e ui ed ith tandem uadru ole mass s ectrometer (Waters evo T -S Micro or e uivalent).

6.10.2 C18 column, 1. m, 0 2.1 mm (Waters Ac uity UP C E or e uivalent)

6.10.3 uard column (Phenomene inete Evo C18 or e uivalent)

6.10.4 Tra delay column (Puros her Star P-18 endca ed 3 µm ibar T 0-4 or e uivalent)

6.11 ottles, DPE or glass, ith linerless DPE or oly ro ylene ca s. arious si es. To store re ared reagents.

7.0 Reagents and standards

7.1 eagents

eagents re ared by the laboratory may be stored in either glass or DPE containers. Pro er cleaning rocedures (Section 4.2) must be follo ed rior to using the containers.

7.1.1 Acetic acid - ACS grade or e uivalent, store at room tem erature

7.1.2 Acetic acid (0.1) - dissolve acetic acid (1 m) in reagent ater (1), store at room tem erature, re lace after 3 months. *This reagent is used only for sample extract dilution.*

7.1.3 Acetonitrile UP C grade or e uivalent, verified before use, store at room tem erature

7.1.4 Ammonium acetate - (Caledon Ultra C MS grade, or e uivalent), store at 2-8 C, re lace 2 years after o ening date

7.1.5 Ammonium hydro ide - certified ACS grade or e uivalent, 30 in ater, store at room tem erature

7.1.6 A ueous ammonium hydro ide (3) - add ammonium hydro ide (10 m , 30) to reagent ater (0 m), store at room tem erature, re lace after 3 months

7.1.7 Methanolic ammonium hydro ide

7.1.7.1 Methanolic ammonium hydro ide (0.3) - add ammonium hydro ide (1 m , 30) to methanol (m), store at room tem erature, re lace after 1 month

7.1.7.2 Methanolic ammonium hydro ide (1) - add ammonium hydro ide (3.3 m , 30) to methanol (m), store at room tem erature, re lace after 1 month

7.1.7.3 Methanolic ammonium hydro ide (2) - add ammonium hydro ide (6.6 m , 30) to methanol (3.4 m), store at room tem erature, re lace after 1 month

7.1.8 Methanolic otassium hydro ide (0.0 M) add 3.3 g of otassium hydro ide to 1 of methanol, store at room tem erature, re lace after 3 months

7.1.9 Methanol ith 4 ater, 1 ammonium hydro ide and 0.62 acetic acid - add ammonium hydro ide (3.3 m , 30), reagent ater (1. m) and acetic acid (0.62 m) to methanol (2 m), store at room tem erature, re lace after 1 month. This solution is used to re are the instrument blan (Section .3.6).

7.1.10 Eluent A Acetonitrile, Caledon Ultra CMS grade or e uivalent

7.1.11 Eluent - 2 mM ammonium acetate in ater acetonitrile. Dissolve 0.1 4 g of ammonium acetate (Section .1.4) in 0 m of ater and 0 m of acetonitrile (Caledon Ultra CMS grade, or e uivalent). Store at room tem erature, shelf life 2 months.

7.1.12 ormic acid - (greater than 6 urity or e uivalent), verified by lot number before use, store at room tem erature

7.1.13 ormic acid

7.1.13.1 ormic acid (a ueous, 0.1 M) - dissolve formic acid (4.6 g) in reagent ater (1), store at room tem erature, re lace after 2 years

7.1.13.2 ormic acid (a ueous, 0.3 M) - dissolve formic acid (13.8 g) in reagent ater (1), store at room tem erature, re lace after 2 years

7.1.13.3 ormic acid (a ueous, v v) - mi m formic acid ith m reagent ater, store at room tem erature, re lace after 2 years

7.1.13.4 ormic acid (a ueous, 0 v v) - mi 0 m formic acid ith 0 m reagent ater, store at room tem erature, re lace after 2 years

7.1.13.5 ormic acid (methanolic 1 1, 0.1 M formic acid methanol) - mi e ual volumes of methanol and 0.1 M formic acid, store at room tem erature, re lace after 2 years

7.1.14 Methanol - (P C grade or better, . urity), verified by lot number before use, store at room tem erature

7.1.15 Potassium hydro ide certified ACS or e uivalent, store at room tem erature, re lace after 2 years

7.1.16 eagent ater aboratory reagent ater, test by lot batch number for residual P AS content

7.1.17 Carbon EnviCarb 1-M-USP or e uivalent, verified by lot number before use, store at room tem erature. oose carbon allo s for better adsor tion of interferent organics.

Note: The single-laboratory validation laboratory achieved better performance with loose carbon than carbon cartridges. Loose carbon will be used for the multi-laboratory validation to set statistically based method criteria. Once the method is multi-laboratory validated, laboratories will have the flexibility to use carbon cartridges as long as all method QC criteria are met.

7.1.18 Toluene P C grade, verified by lot number before use. Store at room tem erature.

7.1.19 Acetone - Pesticide grade, verified by lot number before use in rinsing tissue dissection and rocessing e ui ment.

7.1.20 Dichloromethane (methylene chloride), esticide grade, verified by lot number before use in rinsing tissue dissection and rocessing e ui ment.

7.2 eference matrices Matrices in hich P AS and interfering com ounds are not detected by this method. These matrices are to be used to re are the batch C sam les (e.g., method blan , and ongoing recision and recovery sam le).

7.2.1 eagent ater urified ater, Ty e

7.2.2 Solids reference matri Otta a or reagent-grade sand

7.2.3 Tissue reference matri chic en breast or similar animal tissue

7.3 Standard solutions Pre are from materials of no n urity and com osition or urchase as solutions or mi tures ith certification to their urity, concentration, and authenticity. Observe the safety recautions in Section .

Purchase of commercial standard solutions or mi tures is highly recommended for this method ho ever, hen these are not available, re aration of stoc solutions from neat materials may be necessary. f the chemical urity is 8 or greater, the eight may be used ithout correction to calculate the concentration of the standard. Dissolve an a ro riate amount of assayed reference material in the re uired solvent. or e am le, eigh 10 to 20 mg of an individual com ound to three significant figures in a 10-m ground-glass-sto ered volumetric flas and fill to the mar ith the re uired solvent. Once the com ound is com letely dissolved, transfer the solution to a clean vial and ca .

When not being used, store standard solutions in the dar at less than 4 C unless the vendor recommends other ise in scre -ca ed vials ith foiled-lined ca s. Place a mar on the vial at the level of the solution so that solvent loss by eva oration can be detected. e lace the solution if solvent loss has occurred.

Note: Native PFAS standards are available from several suppliers. Isotopically labeled compounds are available from Cambridge Isotope Laboratories and Wellington Laboratories, but may also be available from other suppliers. Listing of these suppliers does not constitute a recommendation or endorsement for use. All diluted solutions must be stored in glass or HDPE containers that have been thoroughly rinsed with methanol.

^{18}O-mass labeled perfluoroalkyl sulfonates may undergo isotopic exchange with water under certain conditions, which lowers the isotopic purity of the standards over time.

The laboratory must maintain records of the certificates for all standards for traceability ur oses. Co ies of the certificates must be rovided as art of the data ac ages in order to chec that ro er calculations ere erformed.

7.3.1 E tracted nternal Standard (E S) (a. .a. isoto ically labeled com ound) Pre are the E S solution containing the isoto ically labeled com ounds listed in Table 3 as e tracted internal standards in methanol from rime stoc s. An ali uot of E S solution, ty ically 0 , is added to each sam le rior to e traction. Table 3 resents the nominal amounts of E S com ounds added to each sam le. The list of isoto ically labeled com ounds in Table 3 re resents the com ounds that ere available at the time this method as validated. Other isoto ically labeled com ounds may be used as they become available.

7.3.2 Non-E tracted nternal Standard (N S) - The N S solution containing the isoto ically labeled com ounds listed in Table 3 as non-e tracted internal standards is re ared in methanol from rime stoc . An ali uot of N S solution, ty ically 0 , is added to each sam le rior to instrumental analysis. Table 3 resents the nominal amounts of N S com ounds added to each sam le.

7.3.3 Native Standards Solution - Pre are a s i ing solution, containing the method analytes listed in Table 4, in methanol from rime stoc s. The solution is used to re are the calibration standards and to s i e the no n reference C sam les that are analy ed ith every batch. uantitative standards containing a mi ture of branched and linear isomers must be used for method analytes if they are commercially available. Currently, these include P OS, P S, NMe OSAA, and NEt OSAA.

7.3.4 Calibration standard solutions A series of calibration solutions containing the target analytes and the ^{13}C-, ^{18}O-, and deuterium-labeled e tracted internal standards (E S) and non-e tracted internal standards (N S) is used to establish the initial calibration of the analytical instrument. The concentration of the method analytes in the solutions varies to encom ass the or ing range of the instrument, hile the concentrations of the E S and N S remain constant. The calibration solutions are re ared using methanol, methanolic ammonium hydro ide (2), ater, acetic acid and the method analyte and isoto ically labeled com ound standard solutions. After dilution, the final solution ill match the solvent mi of sam le e tracts, hich contain methanol ith 4 ater, 1 ammonium hydro ide and 0.62 acetic acid (Section .1.). Calibration standard solutions do not undergo solid hase e traction cleanu .

Concentrations for seven calibration solutions are resented in Table 4. A minimum of si contiguous calibrations standards are re uired for a valid analysis hen using a linear calibration model, ith at least five of the si calibration standards being ithin the uantitation range (e.g., from the O to the highest calibration standard). f a second-order calibration model is used, then a minimum of seven calibration standards are

re uired, ith at least si of the seven calibration standards ithin the uantitation range. The lo est level calibration standard must meet a signal-to-noise ratio of 3 1 and be at a concentration less than or e ual to the imit of uantitation (O). All initial calibration re uirements listed in Table must be met. An instrument sensitivity chec (SC) standard at the concentration of the lo est calibration standard ithin the uantitation range is re uired to be analy ed at the beginning of the analytical run (Section 10.3.3.1 and Section 13.3). A mid-level calibration solution is analy ed at least every ten sam les or less, on an ongoing basis for the ur ose of calibration verification. A mid-level calibration verification (C) standard must also be analy ed after all sam le analyses in order to brac et the analytical batch.

Note: Additional calibration standards, at levels lower than the lowest calibration standard listed in the method, may be added to accommodate a lower limit of quantitation if the instrument sensitivity allows. Calibration standards at the high end of the calibration may be eliminated if the linearity of the instrument is exceeded or at the low end if those calibration standards do not meet the S/N ratio criterion of 3:1, as long as the required number of calibration points is met. All analytes with commercially available stable isotope analogues must be quantified using isotope dilution.

7.3.5 ualitative Standards - Standards that contain mi tures of the branched and linear isomers of the method analytes and that are used for com arison against sus ected branched isomer ea s in field sam les. These ualitative standards are **not** re uired for those analytes here the uantitative standards in Section .3.3 already contain the branched and linear isomers. ualitative standards that are currently commercially available include P OA, P NA, P OSA, NMe OSA, NEt OSA, NEt OSE, and NMe OSE.

7.3.6 nstrument lan During the analysis of a batch of sam les, a solvent blan is analy ed after sam les containing high level of target com ounds (e.g., calibration, C) to monitor carryover from the revious injection. The injection blan consists of the solution in Section .1. fortified ith the E S and N S for uantitation ur oses.

7.3.7 Stability of solutions Standard solutions used for uantitative ur oses (Sections .3.1 through .3.) should be assayed eriodically (e.g., every 6 months) against certified standard reference materials (S Ms) from the National nstitute of Science and Technology (N ST), if available, or certified reference materials from a source that ill attest to the authenticity and concentration, to assure that the com osition and concentrations have not changed.

7.4 Sodium iodide cesium iodide mass calibration solution 2 mg m Na and 0 μg m Cs in (1 1) iso ro yl alcohol ater (Waters 0000088 , or e uivalent) or other solution, based on manufacturer s s ecifications.

7.5 Taurodeo ycholic Acid (TDCA) or Sodium taurodeo ychloate hydrate (Sigma Aldrich 80221- M, or e uivalent). This com ound is used to evaluate the chromatogra hic rogram relative to the ris of an interference from bile salts in tissue sam les. Pre are solution at a concentration of 100 mg in the same solvent as the calibration standards.

8.0 Sample collection, preservation, storage, and holding times

8.1 Collect samples in HDPE containers following conventional sampling practices (Reference 5). All sample containers must have linerless HDPE or polypropylene caps. Other sample collection techniques, or sample volumes may be used, if documented.

8.2 Aqueous samples

8.2.1 Samples that flow freely are collected as grab samples or in refrigerated bottles using automatic sampling equipment. Collect 500 mL of sample (other than leachates) in an HDPE bottle. Do not fill the bottle past the shoulder, to allow room for expansion during frozen storage.

Note: Collect at least two aliquots of all aqueous samples to allow sufficient volume for the determination of percent solids and for pre-screening analysis. That second aliquot may be collected in a smaller sample container (e.g., 250-mL or 125-mL).

Because the target analytes are known to bind to the interior surface of the sample container, the entire aqueous sample that is collected must be prepared and analyzed and subsampling avoided whenever possible. Therefore, if a sample volume smaller than 500 mL is to be used for analysis, collect the sample in an appropriately sized HDPE container.

8.2.2 Leachate samples from landfills can present significant challenges and therefore only 100 mL of sample is collected for the analysis. Collect two 100-mL leachate sample aliquots in a similar manner as described in Section 8.2.1, using appropriately sized containers.

8.2.3 Maintain all aqueous samples protected from light at 0 - 6 ºC from the time of collection until shipped to the laboratory. Samples must be shipped as soon as practical with sufficient ice to maintain the sample temperature below 6 ºC during transport and be received by the laboratory within 48 hours of collection. The laboratory must confirm that the sample temperature is 0 - 6 ºC upon receipt. Once received by the laboratory, the samples must be stored at ≤ -20 ºC until sample preparation.

8.3 Solid (soil, sediment, biosolid), excluding tissue

8.3.1 Collect samples as grab samples using wide-mouth jars and fill no more than ¾ full (see Section 6.1.1.2 for container size and type).

8.3.2 Maintain solid samples protected from light (in HDPE containers) at 0 - 6 ºC from the time of collection until receipt at the laboratory. The laboratory must confirm that the sample temperature is 0 - 6 ºC upon receipt. Once received by the laboratory, the samples must be stored at ≤ -20 ºC until sample preparation.

8.4 Fish and other tissue samples

The nature of the tissues of interest may vary by project. Field sampling plans and protocols should explicitly state the samples to be collected and if any processing will be conducted in the field (e.g., filleting of whole fish or removal of organs). All field procedures must involve materials and equipment that have been shown to be free of PFAS.

8.4.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.4.2 If whole fish are collected, wrap the fish in aluminum foil or food-grade polyethylene tubing, and maintain at 0 - 6 ºC from the time of collection until receipt at the laboratory, to a maximum time of 24 hours. If a longer transport time is necessary, freeze the sample before shipping. Ideally, fish should be frozen upon collection and shipped to the laboratory on dry ice.

8.4.3 Once received by the laboratory, the samples must be maintained protected from light at ≤ -20 ºC until prepared. Store unused samples in HDPE containers or wrapped in aluminum foil at ≤ -20 ºC.

8.5 Holding times

8.5.1 Aqueous samples (including leachates) should be analyzed as soon as possible; however, samples may be held in the laboratory for up to 90 days from collection, when stored at ≤ -20 ºC and protected from the light. When stored at 0 - 6 ºC and protected from the light, aqueous samples may be held for up to 28 days, with the caveat that issues were observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days. These issues are more likely to elevate the observed concentrations of other PFAS compounds via the transformation of these precursors if they are present in the sample.

8.5.2 Solid samples (soils and sediments) and tissue samples may be held for up to 90 days, if stored by the laboratory in the dark at either 0 - 6 ºC or ≤ -20 ºC, with the caveat that samples may need to be extracted as soon as possible if NFDHA is an important analyte.

8.5.3 Biosolids samples may be held for up to 90 days, if stored by the laboratory in the dark at 0 - 6 ºC or at -20 ºC. Because microbiological activity in biosolids samples at 0 - 6 ºC may lead to production of gases which may cause the sample to be expelled from the container when it is opened, as well as producing noxious odors, EPA recommends that samples be frozen if they need to be stored for more than a few days before extraction.

8.5.4 Store sample extracts in the dark at less than 0 - 4 ºC until analyzed. If stored in the dark at less than 0 - 4 ºC, sample extracts may be stored for up to 90 days, with the caveat that issues were observed for some ether sulfonates after 28 days. These issues may elevate the observed concentrations of the ether sulfonates in the extract over time. Samples may need to be extracted as soon as possible if NFDHA is an important analyte.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 6). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with isotopically labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied to a sample matrix other than water (e.g., soils, biosolids, tissue), the appropriate alternative reference matrix (Sections 7.2.2 - 7.2.3) is substituted for the reagent water matrix (Section 7.2.1) in all performance tests.

9.1.1 The laboratory must ma e an initial demonstration of the ability to generate acce table recision and recovery ith this method. This demonstration is given in Section .2.

9.1.2 n recognition of advances that are occurring in analytical technology, and to overcome matri interferences, the laboratory is ermitted certain o tions to im rove se arations or lo er the costs of measurements. These o tions include alternative e traction, concentration, and cleanu rocedures, and changes in sam le volumes, columns, and detectors. Alternative determinative techni ues and changes that degrade method erformance, are *not* allo ed ithout rior revie and a roval.

Note: For additional flexibility to make modifications without prior EPA review, see 40 CFR Part 136.6.

9.1.2.1 Each time a modification is made to this method, the laboratory is re uired to re eat the rocedure in Section .2. f calibration ill be affected by the change, the instrument must be recalibrated er Section 10. Once the modification is demonstrated to roduce results e uivalent or su erior to results roduced by this method as ritten, that modification may be used routinely thereafter, so long as the other re uirements in this method are met (e.g., isoto ically labeled com ound recovery).

9.1.2.2 The laboratory is re uired to maintain records of any modifications made to this method. These records include the follo ing, at a minimum

a) The names, titles, business addresses, and tele hone numbers of the analyst(s) that erformed the analyses and modification, and of the uality control officer that itnessed and ill verify the analyses and modifications.

b) A listing of ollutant(s) measured, by name and CAS egistry number.

c) A narrative stating reason(s) for the modifications (see Section 1.6).

d) esults from all uality control (C) tests com aring the modified method to this method, including

i. Calibration (Section 10)
ii. Calibration verification (Section 14.3)
iii. nitial recision and recovery (Section .2.1)
iv. soto ically labeled com ound recovery (Section .3)
v. Analysis of blan s (Section .)
vi. Accuracy assessment (Section .4)

e) Data that ill allo an inde endent revie er to validate each determination by tracing the instrument out ut (ea height, area, or other signal) to the final result. These data are to include

i. Sam le numbers and other identifiers
ii. E traction dates
iii. Analysis dates and times
iv. Analysis se uence run chronology
v. Sam le eight or volume (Section 11)
vi. E tract volume rior to each cleanu ste (Section 12)

vii. E tract volume after each cleanu ste (Section 12)
viii. inal e tract volume rior to injection (Section 12)
i . njection volume (Section 13.3)
. Dilution data, differentiating bet een dilution of a sam le or e tract (Section 1 .3)
i. nstrument
ii. Column (dimensions, li uid hase, solid su ort, film thic ness, etc.)
iii. O erating conditions (tem eratures, tem erature rogram, flo rates)
iv. Detector (ty e, o erating conditions, etc.)
v. Chromatograms, rinter ta es, and other recordings of ra data
vi. uantitation re orts, data system out uts, and other data to lin the ra data to the results re orted

9.1.2.3 Alternative columns and column systems f a column or column system other than those s ecified in this method is used, that column or column system must meet all the re uirements of this method.

Note: *The use of alternative columns or programs will likely result in a different elution order.*

9.1.3 Analyses of method blan s are re uired on an on-going basis to demonstrate the e tent of bac ground contamination in any reagents or e ui ment used to re are and analy e field sam les (Section 4.3). The rocedures and criteria for analysis of a method blan are described in Section . .

9.1.4 The laboratory must s i e all sam les ith isoto ically labeled com ounds to monitor method erformance. This test is described in Section .3. When results of these s i es indicate aty ical method erformance for sam les, the sam les are diluted to evaluate hether the erformance issue is caused by the sam le matri . Procedures for dilution are given in Section 1 .3.

9.1.5 The laboratory must, on an ongoing basis, demonstrate that the analytical system is in control through calibration verification and the analysis of ongoing recision and recovery standards (OP), s i ed at lo (OP) and mid-level, and blan s. These rocedures are given in Sections 14.1 through 14. .

9.1.6 The laboratory must maintain records to define the uality of data generated. Develo ment of accuracy statements is described in Section .4.

9.2 nitial Demonstration of Ca ability

9.2.1 nitial recision and recovery (P) To establish the ability to generate acce table recision and recovery, the laboratory must erform the follo ing o erations for each sam le matri ty e to hich the method ill be a lied by that laboratory.

9.2.1.1 E tract, concentrate, and analy e four ali uots of the matri ty e to be tested (Section .2.1 through .2.3), s i ed ith 200 of the native standard solution (Section .3.3), 0 of the E S solution (Section .3.1), and 0 of N S solution (Section .3.2). At least one method blan , matching the matri being analy ed, must be re ared ith the P batch. n the event that more than one M as re ared and analy ed ith the P batch, all blan results must be re orted. All sam le rocessing ste s that are to be used for rocessing sam les,

including re aration and e traction (Sections 11.2 11.4), cleanu (Section 12.0) and concentration (Section 12.0), must be included in this test.

9.2.1.2 Using results of the set of four analyses, com ute the average ercent recovery ( ) of the e tracts and the relative standard deviation (SD) of the concentration for each target and E S com ound.

9.2.1.3 or each native and isoto ically labeled com ound, com are SD and recovery ith the corres onding limits for initial recision and recovery in Table . f SD and for all com ounds meet the acce tance criteria, system erformance is acce table, and analysis of blan s and sam les may begin. f, ho ever, any individual SD e ceeds the recision limit or any individual falls outside the range for recovery, system erformance is unacce table for that com ound. Correct the roblem and re eat the test (Section .2).

9.2.2 Method detection limit (MD) - Each laboratory must also establish MD s for all the analytes using the MD rocedure at 40 C Part 136, A endi . An MD determination must be erformed for all com ounds. The minimum level of uantification (M) is then calculated by multi lying the MD by 3.18 and rounding the result to the nearest 1, 2 or 10^n, here n is ero or an integer. E am le matri -s ecific detection limits are listed in Table 6.

9.3 To assess method erformance on the sam le matri , the laboratory must s i e all sam les ith the isoto ically labeled com ound standard solution (Section .3.1) and all sam le e tracts ith the N S s i ing solution (Section .3.2).

9.3.1 Analy e each sam le according to the rocedures in Sections 11.0 through 16.0.

9.3.2 Com ute the ercent recovery of the isoto ically labeled com ound using the non-e tracted internal standard method (Section 1 .2) and the e uation in Section 14. .2.

9.3.3 The recovery of each isoto ically labeled com ound must be ithin the limits in Tables 9 and 10 (*once the tables are finalized*). If the recovery of any com ound falls outside of these limits, method erformance is unacce table for that com ound in that sam le. Additional cleanu rocedures must then be em loyed to attem t to bring the recovery ithin the normal range. f the recovery cannot be brought ithin the normal range after all cleanu rocedures have been em loyed, ater sam les are diluted, and smaller amounts of soils, biosolids, sediments, and other matrices are re ared and analy ed, er Section 1 .3.

9.4 ecovery of isoto ically labeled com ounds from sam les must also be assessed and records maintained.

9.4.1 After the analysis of 30 sam les of a given matri ty e (ater, soil, biosolids, tissues, etc.) for hich the isoto ically labeled com ounds ass the tests in Section .3, com ute the and the standard deviation of the ercent recovery (S) for the isoto ically labeled com ounds only. E ress the assessment as a ercent recovery interval from - 2S to 2S for each matri . or e am le, if 0 and S 10 for five analyses of soil, the recovery interval is e ressed as 0 to 110 .

9.4.2 U date the accuracy assessment for each isoto ically labeled com ound in each matri on a regular basis (e.g., after each five to ten ne measurements).

9.5 Method blan s A method blan is analy ed ith each sam le batch (Section 4.3) to demonstrate freedom from contamination. The matri for the method blan must be similar to the sam le matri for the batch (e.g., reagent ater blan Section .2.1 , solids matri blan Section .2.2 , or tissue blan Section .2.3).

9.5.1 Analy e the cleaned e tract (Section 12.0) of the method blan ali uot before the analysis of the OP s (Section 14.).

9.5.2 f any P AS is found in the blan at 1) at a concentration greater than the M for the analyte, 2) at a concentration greater than one-third the regulatory com liance limit, or 3) at a concentration greater than one-tenth the concentration in a sam le in the e traction batch, hichever is greatest, analysis of sam les must be halted, and the roblem corrected. Other roject-s ecific re uirements may a ly therefore, the laboratory may ado t more stringent acce tance limits for the method blan at their discretion. f the contamination is traceable to the e traction batch, sam les affected by the blan must be re-e tracted and analy ed, rovided enough sam le volume is available and the sam le are still ithin holding time.

f, continued re-testing results in re eated blan contamination, the laboratory must document and re ort the failures (e.g., as ualifiers on results), unless the failures are not re uired to be re orted as determined by the regulatory control authority. esults associated ith blan contamination for an analyte regulated in a discharge cannot be used to demonstrate regulatory com liance. C failures do not relieve a discharger or ermittee of re orting timely results.

9.6 The s ecifications contained in this method can be met if the a aratus used is calibrated ro erly and then maintained in a calibrated state. The standards used for initial calibration (Section 10.3), calibration verification (Sections 14.2 and 14.3), and for initial (Section .2.1) and ongoing (Section 14.) recision and recovery may be re ared from the same source ho ever, the use of a secondary source for calibration verification is highly recommended henever available. f standards from a different vendor are not available, a different lot number from the same vendor can be considered a secondary source. A C-MS MS instrument ill rovide the most re roducible results if dedicated to the settings and conditions re uired for determination of P AS by this method.

9.7 De ending on s ecific rogram re uirements, field re licates may be collected to determine the recision of the sam ling techni ue, and s i ed sam les may be re uired to determine the accuracy of the analysis hen the e tracted internal standard method is used.

9.8 Matri s i es generally are not re uired for isoto e dilution methods because any deleterious effects of the matri should be evident in the recoveries of the isoto ically labeled com ounds s i ed into every sam le. o ever, because some of the com ounds are uantified by a non-analogous isoto ically labeled com ounds (e.g., P PeS is uantified by $^{13}C_3$-P S), the analysis of matri s i e sam les may hel diagnose matri interferences for s ecific com ounds.

10.0 Calibration and Standardization

10.1 Mass Calibration

The mass s ectrometer must undergo mass calibration to ensure accurate assignments of m s by the instrument. This mass calibration must be erformed at least annually to maintain instrument

sensitivity and stability. Mass calibration must be re eated on an as-needed basis (e.g., C failures, ion masses fall outside of the instrument re uired mass indo , major instrument maintenance, or if the instrument is moved). Mass calibration must be erformed using the calibration com ounds and rocedures rescribed by the manufacturer. The rocedures used for mass calibration and mass calibration verification must evaluate an ion range that encom asses the ion range (1 and 2 m) of the analytes of interest of this method (Table 2).

Multi le eaction Monitoring (M M) analysis is re uired to achieve better sensitivity than full-scan analysis. The ions to be monitored (1 and 2 m) for each native com ound, isoto ically labeled com ound, and N S are given in Table 2.

10.1.1 During the develo ment of this method, instrumental arameters ere o timi ed for the recursor and roduct ions listed on Table 2. Product ions other than those listed may be selected ho ever, the use of ions ith lo er mass or common ions that may not rovide sufficient discrimination bet een analytes of interest and co-eluting interferences must be avoided.

10.1.2 O timi e the res onse of the recursor ion M- ⁻ or M-CO_2 for each method analyte follo ing the manufacturer s guidance. MS arameters (e.g., source voltages, source and desolvation tem eratures, gas flo , etc.) must be methodically changed until o timal analyte res onses are determined. Ty ically, carbo ylic acids have similar MS MS conditions and sulfonic acids have similar MS MS conditions. o ever, since analytes may have different o timal arameters, some com romise on the final o erating conditions may be re uired.

10.1.3 Establish suitable o erating conditions using the manufacturer s instructions and use the table belo for the MS conditions used during the develo ment of this method as guidance.

Operating Conditions for Waters Acquity UPLC, TQ-S Xevo MS/MS

Injection volume	2.0 (This is the default volume, and may be changed to im rove erformance)	
MS/MS Conditions	Source Tem (C)	140
	Desolvation Tem (C)	00
	Ca illary oltage ( )	0. 0
	Cone as (h)	0
	Desolvation gas (h)	800

10.1.4 n the absence of manufacturer-s ecific instructions and acce tance criteria, the follo ing rocedure may be used for mass calibration.

10.1.4.1 ntroduce the NaCs calibration solution (Section .4) to the MS at the flo rate necessary to roduce a stable aerosol s ray (e.g., 10 µ min).

10.1.4.2 Scan the MS MS over the mass range from 20 to 3000 atomic mass units (amu) (or Daltons Da). Adjust the source arameters to o timi e ea intensity and sha e across the mass range. The e act m s for NaCs calibration are

Calibration Masses (Daltons)

22. 8 8	22.3 2	1 1.614
132. 0 4	10 2.24 4	2121. 0 1
1 2.8840	1222.143	22 1.4033
322. 82	13 2.03	2421.2 6
4 2.6 2	1 21. 321	2 1.1 18
622. 66	16 1.8264	2 21.0861
2.4610	1821. 206	28 0. 803

10.1.4.3 Mass calibration is judged on the basis of the resence or absence of the e act calibration masses (e.g., a limit of the number of masses that are missed). Absent vendor-s ecific instructions, all masses from 22. 8 8 to 1 1.614 must be resent. f ea s in this range are missing or not correctly identified, adjust the MS MS, and re eat the test. Only after the MS MS is ro erly calibrated may standards, blan s, and sam les be analy ed.

10.1.4.4 Mass s ectrometer o timi ation Prior to measurements of a given analyte the mass s ectrometer must be se arately o timi ed for that analyte.

10.1.4.5 Using the ost-column um , se arately infuse a solution containing 2 - g m of each com ound in methanol into the MS.

10.1.4.6 O timi e sensitivity to the roduct ion m for each com ound. Precursor-roduct ion m s other than those listed may be used rovided re uirements in this method are met.

10.1.4.7 After MS calibration and o timi ation and C-MS MS calibration, the same C-MS MS conditions must be used for analysis of all standards, blan s, P and OP standards, and sam les.

10.1.5 Mass Calibration erification

A mass calibration verification must be erformed follo ing mass calibration, rior to standards and sam les analysis. Mass verification chec s must also be erformed after any subse uent mass calibrations. Each laboratory must follo the instructions for their individual instrument soft are to confirm the mass calibration, mass resolution and ea relative res onse. Mass calibration verification must be erformed using standards hose mass range brac ets the masses of interest (uantitative and ualitative ions).

10.1.5.1 Chec the instrument mass resolution to ensure that it is at least unit resolution. nject a mid-level CA standard under C-MS MS conditions to obtain the retention times of each method analyte. Divide the chromatogram into retention time indo s each of hich contains one or more chromatogra hic ea s. During MS MS analysis, fragment a small number of selected recursor ions (M- -) for the analytes in each indo and choose the most abundant roduct ion. The roduct ions (also the uantitation ions) chosen during method develo ment are in Table 2, although these ill be instrument de endent. Unit resolution is demonstrated hen the value of the ea idth at half-height is ithin 0. 0.1 amu or Da.

10.1.5.2 Chec the mass calibration by measuring the amount of ea drift from the e ected masses. f the ea a e has shifted more than a ro imately 0.1 Da, then the instrument ill need to be recalibrated follo ing the manufacturer s instructions.

10.2 Chromatogra hic conditions

10.2.1 The chromatogra hic conditions should be o timi ed for com ound se aration and sensitivity. The same o timi ed o erating conditions must be used for the analysis of all standards, blan s, P and OP standards, and sam les. The follo ing table gives the suggested chromatogra hic conditions for this method using the s ecified instrument and column. Different instruments may re uire slightly different o erating conditions. **Modification of the solvent composition of the standard or extract by increasing the aqueous content to prevent poor peak shape is not permitted.** The ea sha e of early eluting com ounds may be im roved by increasing the volume of the injection loo or increasing the a ueous content of the initial mobile hase com osition.

General LC Conditions

Column Temp (°C)	40
Max Pressure (bar)	1100.0

LC Gradient Program

Time (min)	Flow mixture [1,2]	Flow Rate Program	Gradient Curve
0.0	2 eluent A, 8 eluent	0.3 m min	nitial
0.2	2 eluent A, 8 eluent	0.3 m min	2
4.0	30 eluent A, 0 eluent	0.40 m min	
	eluent A, 4 eluent	0.40 m min	8
	eluent A, 2 eluent	0.40 m min	8
10	eluent A, eluent	0.40 m min	6
10.4	2 eluent A, 8 eluent	0.40 m min	10
11.8	2 eluent A, 8 eluent	0.40 m min	
12.0	2 eluent A, 8 eluent	0.3 m min	1

[1] Eluent A Acetonitrile

[2] Eluent 2 mM ammonium acetate in ater acetonitrile

Note: LC system components, as well as the mobile phase constituents, may contain many of the analytes in this method. Thus, these PFAS will build up on the head of the LC column during mobile phase equilibration. To minimize the background PFAS peaks and to keep baseline levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). In addition, priming the mobile phase and flushing the column with at least 90% methanol before initiating a sequence may reduce background contamination.

10.2.2 etention time calibration

10.2.2.1 nject com ound solution(s) to determine its retention time. The laboratory may ant to inject com ounds se arately the first time they erform the calibration. All native com ounds for hich there is an isoto ically labeled analog ill elute slightly before or ith the labeled analog. Store the retention time (T) for each com ound in the data system.

10.2.2.2 Once T indo s have been confirmed for each analyte, once er CA and at the beginning of the analytical se uence, the osition of each method analyte, E S analyte, and N S analyte ea s shall be set using the mid oint standard of the CA curve hen CA is erformed. When CA is not erformed, the initial C retention times or the mid oint standard of the CA curve can be used to establish the T indo osition.

10.2.2.3 Method analyte, E S analyte, and N S analyte Ts must fall ithin 0.4 minutes of the redicted retention times from the mid oint standard of the CA or initial daily C , hichever as used to establish the T indo osition for the analytical batch. All branched isomer ea s identified in either the calibration standard or the ualitative (technical grade) standard must fall ithin in the retention time indo for that analyte.

10.2.2.4 or all method analytes ith e act corres onding isoto ically labeled analogs, method analytes must elute ithin 0.1 minutes of the associated E S.

10.2.2.5 When establishing the chromatogra hic conditions, it is im ortant to consider the otential interference of bile salts during analyses of tissue sam les. nject a standard containing TDCA (Section .) during the retention time calibration rocess and adjust the conditions to ensure that TDCA does not coelute ith any of the target analytes, E S, or N S standards. Analytical conditions must be set to allo a se aration of at least 1 minute bet een the bile salts and P OS.

10.3 nitial calibration

nitial calibration is erformed using a series of at least si solutions, ith at least five of the si calibration standards being ithin the uantification. (f a second-order calibration model is used, then one additional concentration is re uired.) The initial calibration solutions contain the entire suite of isoto ically labeled com ounds, N Ss, and target com ounds. Calibration is verified ith a calibration verification (C) standard at least once every ten field sam les or less, by analysis of a mid-level calibration solution. Calibration verification uses the mean s or s determined from the initial calibration to calculate the analyte concentrations in the verification standard.

Note: Six calibration standards is the minimum number that must be used in the initial calibration; however, the laboratory may use more standards, as long as the criteria in Section 10.3.3.3 can be met.

Prior to the analysis of sam les, and after the mass calibration chec has met all criteria in Section 10.1.4, each C-MS MS system must be calibrated at a minimum of 6 standard concentrations (Section .3.4 and Table 4). This method rocedure calibrates and uantifies 40 P AS target analytes, using the isoto ically labeled com ounds added to the sam le rior to e traction, by one of t o a roaches

- True isoto e dilution uantification (D), hereby the res onse of the target com ound is com ared to the res onse of its isoto ically labeled analog. T enty-four target com ounds are uantified in this ay.

- E tracted internal standard uantification (E S), hereby the res onse of the target com ound is com ared to the res onse of the isoto ically labeled analog of another com ound ith chemical and retention time similarities. Si teen target com ounds are uantified in this ay.

10.3.1 nitial calibration fre uency

Each C-MS MS system must be calibrated henever the laboratory ta es corrective action that might change or affect the initial calibration criteria, or if either the C or nstrument Sensitivity Chec (SC) acce tance criteria have not been met.

10.3.2 nitial calibration rocedure

Pre are calibration standards containing the native com ounds, E Ss, and N Ss, at the concentrations described in Table 4. Analy e each calibration standard by injecting 2.0 (this volume may be changed to im rove erformance).

Note: The same injection volume must be used for all standards, samples, blanks, and QC samples.

10.3.3 nitial calibration calculations

10.3.3.1 nstrument sensitivity

Sufficient instrument sensitivity is established if a signal-to-noise ratio ≥ 3:1 can be achieved hen analy ing the lo est concentration standard ithin the uantitation range that the laboratory includes in its assessment of calibration linearity (Table 4).

10.3.3.2 es onse atios ( ) and es onse actors ( )

The res onse ratio ( ) for each com ound calibrated by isoto e dilution is calculated according to the e uation belo , se arately for each of the calibration standards, using the areas of the uantitation ions (1) ith the m sho n in Table 2. is used for the 24 com ounds uantified by true isoto e dilution.

$$RR = \frac{Area_n\, M_l}{Area_l\, M_n}$$

here

$Area_n$ The measured area of the 1 m for the native (unlabeled) P AS

$Area_l$ The measured area at the 1 m for the corres onding isoto ically labeled P AS added to the sam le before e traction

M_l The mass of the isoto ically labeled com ound in the calibration standard

M_n The mass of the native com ound in the calibration standard

Similarly, the res onse factor ( ) for each unlabeled com ound calibrated by e tracted internal standard is calculated according to the e uation belo . is used for the 16 com ounds uantified by e tracted internal standard.

$$RF = \frac{Area_s\, M_{EIS}}{Area_{EIS}\, M_s}$$

here

$Area_s$ The measured area of the 1 m for the target (unlabeled) P AS

$Area_{E\ S}$ The measured area at the 1 m for the isoto ically labeled P AS used as the e tracted internal standard (E S)

M_{ES} The mass of the isoto ically labeled P AS used as the e tracted internal standard (E S) in the calibration standard

M_s The mass of the target (unlabeled) P AS in the calibration standard

A res onse factor ($_s$) is calculated for each isoto ically labeled com ound in the calibration standard using the e uation belo . $_s$ is used for the 24 isoto ically labeled com ounds uantified by non-e tracted internal standard.

$$RF_s = \frac{Area_l \, M_{NIS}}{Area_{NIS} \, M_l}$$

here

$Area_l$ The measured area of the 1 m for the isoto ically labeled P AS standard added to the sam le before e traction

$Area_{NS}$ The measured area at the 1 m for the isoto ically labeled P AS used as the non-e tracted internal standard (N S)

M_{NS} The mass of the isoto ically labeled com ound used as the non-e tracted internal standard (N S) in the calibration standard

M_l The mass of the isoto ically labeled P AS standard added to the sam le before e traction

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Note: Other calculation approaches may be used, such as linear regression or non-linear regression based on the capability of the data system used by the laboratory.

10.3.3.3 nstrument inearity

One of the follo ing t o a roaches must be used to evaluate the linearity of the instrument calibration

O tion 1 Calculate the relative standard deviation (SD) of the or values of the si initial calibration standards for each native com ound and isoto ically labeled com ound. The SD must be ≤ 20% to establish instrument linearity.

O tion 2 Calculate the relative standard error (SE) of the si initial calibration standards for each native com ound and isoto ically labeled com ound. The RSE for all method analytes must be ≤ 20 to establish instrument linearity.

10.3.4 nitial calibration corrective actions

f the instrument sensitivity or the instrument linearity criteria for initial calibration are not met, ins ect the system for roblems and ta e corrective actions to achieve the criteria. This may re uire the re aration and analysis of fresh calibration standards. All initial calibration criteria must be met before any sam les or re uired blan s are analy ed.

10.3.5 ile salts interference chec

The laboratory must analy e a TDCA standard after the initial calibration, rior to the analysis of tissue sam les, to chec for interferences caused by bile salts. f an interference is resent, the chromatogra hic conditions must be modified to eliminate the interference from TDCA (e.g., changing the retention time of TDCA such that it falls outside the

retention indo for P OS by at least one minute), and the initial calibration re eated. f tissue sam le analyses are not being conducted, this chec may be s i ed.

11.0 Sample preparation and extraction

or a ueous sam les that contain articles and solid sam les, ercent solids are determined using the rocedures in Section 11.1. This section describes the sam le re aration rocedures for a ueous sam les ith 0 mg solids (Section 11.2), solid (soil, sediment or biosolid) sam les (Section 11.3) and tissue sam les (Section 11.4).

Note: It is highly recommended that the laboratory pre-screens all samples prior to performing the analysis (see Appendix A). For aqueous samples, use the secondary container provided for percent solids to perform the pre-screening. If high levels of PFAS are present in the sample, a lower volume is required for analysis.

The laboratory may subsample the aqueous samples as described in Appendix B; however, subsampling must meet project-specific requirements. The laboratory must notify the client before proceeding with subsampling. Once the laboratory becomes familiar with the levels of PFAS in the samples for their clients, the samples should be collected in the appropriate sample container size to avoid subsampling. The sample data report must state when subsampling has been employed.

Do not use any fluoropolymer articles or task wipes in these extraction procedures. Use only HDPE or polypropylene wash bottles and centrifuge tubes. Reagents and solvents for cleaning syringes may be kept in glass containers.

11.1 Determination of Percent Solids

11.1.1 Determination of ercent sus ended solids A ueous li uids and multi- hase sam les consisting of mainly an a ueous hase

11.1.1.1 Desiccate and eigh a glass fiber filter (Section 6.4.3) to three significant figures.

11.1.1.2 ilter 10.0 0.02 m of ell-mi ed sam le through the filter.

11.1.1.3 Dry the filter a minimum of 12 hours at 110 C and cool in a desiccator.

11.1.1.4 Calculate ercent solids as follo s

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying\ (g) - weight\ of\ filter\ (g)}{10\ g}\ x\ 100$$

11.1.2 Solids (e cluding tissues)

11.1.2.1 Weigh to 10 g of sam le to three significant figures in a tared bea er.

11.1.2.2 Dry a minimum of 12 hours at 110 C, and cool in a desiccator.

11.1.2.3 Calculate ercent solids as follo s

$$\% \, solids = \frac{weight \, of \, sample \, aliquot \, after \, drying \, (g)}{weight \, of \, sample \, aliquot \, before \, drying \, (g)} \, x \, 100$$

11.2 A ueous Sam le Processing

This method is a licable to a ueous sam les containing u to 0 mg of sus ended solids er sam le. The rocedure re uires the re aration of the entire sam le. Smaller sam le volumes may be analy ed for sam les containing solids greater than s ecified for this method, or hen unavoidable due to high level of P AS ho ever, subsam ling should be avoided henever ossible. Ty ical sam le si e is 00 m ho ever, sam le si e may be u to 1000 m . The sam le is to be analy ed in its entirety and should not be filtered. eachate sam les are analy ed using a 100-m sam le volume. Therefore, they must not be included in the same sam le re aration batch as a ueous sam les analy ed hich are analy ed using 00-m sam le volumes.

11.2.1 omogeni e the sam le by inverting the sam le 3 4 times and allo ing the sam le to settle. Do not filter the sam le. The standard rocedure is to analy e the entire sam le, lus a basic methanol rinse of the container.

11.2.2 The volume of the a ueous sam le analy ed is determined by eighing the full sam le bottle and then the em ty sam le bottle (see Section 12.2). Weigh each sam le bottle (ith the lid) to 0.1 g.

11.2.3 Pre are a method blan and t o OP s using P AS-free ater in DPE bottles. Select a volume of ater that is ty ical of the sam les in the batch. S i e one OP sam le ith native standard solution (Section .3.3) at 2 the O (OP). This ali uot ill serve to verify the O . S i e the other OP sam le at the concentration of the mid-level calibration oint. This ali uot ill serve as the traditional OP .

Note: If matrix spikes are required for a specific project, spike the field sample bottles designated for use as MS/MSD samples with native standard solution (Section 7.3.3) at a concentration 3 to 5 times the background concentration determined during screening of the unspiked sample. If screening was not performed, then spike those samples at the concentration of the mid-level calibration point.

11.2.4 S i e an ali uot of E S solution (Section .3.1) directly into the sam le in the original bottle (or subsam led bottle) as ell as to the bottles re ared for the C sam les. Mi by s irling the sam le container.

11.2.5 Chec that the is 6. 0. . f necessary, adjust ith 0 formic acid (Section .1.13.4) or ammonium hydro ide (or ith formic acid Section .1.13.3 and 3 a ueous ammonium hydro ide Section .1.6.2). The e tract is no ready for solid- hase e traction (SPE) and cleanu (Section 12.0).

11.3 Solid Sam le (e cluding tissues) Processing

Use a stainless s oon to mi the sam le in its original jar. f it is im ractical to mi the sam le ithin its container transfer the sam le to a larger container. emove roc s, invertebrates, and foreign objects. egetation can either be removed from the sam le before homogeni ation or cut into small ieces and included in the sam le, based on roject re uirements. Mi the sam le thoroughly, stirring from the bottom to the to and in a circular motion along the sides of the jar, brea ing articles to less than 1 mm by ressing against the side of the container. The homogeni ed sam le should be even in colour and have no se arate layers. Store the homogeni ed material in its

original container or in multi le smaller containers. Determine the ercent solids as er Section 11.1.2.

Note: The maximum sample weight for sediment or soil is 5 g dry weight. The maximum sample weight for biosolids is 0.5 g dry weight.

Small amounts of reagent free water used for method blanks (10% of sample weight or less) can be added to unusually dry samples. This is an option, not a requirement.

11.3.1 Weigh out an ali uot of solid sam le, not dried (ali uot should rovide g dry eight for soil and sediment or 0. g dry- eight for biosolids) into a 0-m oly ro ylene centrifuge tube. ecause biosolids sam les are analy ed ith a 0. -g sam le, they must not be included in the same sam le re aration batch as solid sam les analy ed ith -g sam le masses.

11.3.2 Pre are batch C sam les using g of reference solid (Section .2.2) etted ith 2. g of reagent ater for the method blan and t o OP s (use 0. g of reference solid ith 0.2 g of reagent ater for biosolid sam le batches). The addition of reagent ater to the sand rovides a matri closer in com osition to real- orld sam les. S i e one OP sam le ith native standard solution (Section .3.3) at 2 the O (OP). This ali uot ill serve to verify the O . S i e the other OP sam le at the concentration of the mid-level calibration oint. This ali uot ill serve as the traditional OP .

Note: If matrix spikes are required for a specific project, spike the field sample aliquots designated for MS/MSD samples with native standard solution (Section 7.3.3) at the concentration 3 to 5 times the background concentration determined during screening of the unspiked sample. If screening was not performed, then spike those samples at the concentration of the mid-level calibration point.

11.3.3 S i e an ali uot of E S solution (Section .3.1) directly into each centrifuge tube containing the ali uoted field and C sam les. orte the sam le to dis erse the standard and allo to e uilibrate for at least 30 minutes.

11.3.4 Add 10 m of 0.3 methanolic ammonium hydro ide (Section .1. .1) to each centrifuge tube. orte to dis erse, then sha e for 30 minutes on a variable s eed mi ing table. Centrifuge at 2800 r m for 10 minutes and transfer the su ernatant to a clean 0-m oly ro ylene centrifuge tube.

11.3.5 Add 1 m of 0.3 methanolic ammonium hydro ide (Section .1. .1) to the remaining solid sam le in each centrifuge tube. orte to dis erse, then sha e for 30 minutes on a variable s eed mi ing table. Centrifuge at 2800 r m for 10 minutes and decant the su ernatant from the second e traction into the centrifuge tube ith the su ernatant from the first e traction.

11.3.6 Add another m of 0.3 methanolic ammonium hydro ide (Section .1. .1) to the remaining sam le in each centrifuge tube. Sha e by hand to dis erse, centrifuge at 2800 r m for 10 minutes and decant the su ernatant from the third e traction into the centrifuge tube ith su ernatant from the first and second e tractions.

11.3.7 Using a 10-mg scoo , add 10 mg of carbon (Section .1.1) to the combined e tract, mi by occasional hand sha ing for no more than five minutes and then centrifuge at 2800 r m

for 10 minutes. mmediately decant the e tract into a 60-m glass eva oration or concentrator tube.

11.3.8 Dilute to a ro imately 3 m ith reagent ater. A se arate concentrator tube mar ed at the 3 -m level may be e t for a visual reference to get the a ro imate volume. Sam les containing more than 0 ater may yield e tracts that are greater than 3 m in volume therefore, do not add ater to these. Determine the ater content in the sam le as follo s (ercent moisture is determined from the solids)

$$Water\ Content\ in\ Sample = \frac{Sample\ Weight\ (g) \times Moisture\ (\%)}{100}$$

11.3.9 Concentrate each e tract at a ro imately C ith a N_2 flo of a ro imately 1.2 min to a final volume that is based on the ater content of the sam le (*see table below*). Allo e tracts to concentrate for 2 minutes, then mi (by vorte if the volume is 20 m or using a glass i ette if the volume is 20 m). Continue concentrating and mi ing every 10 minutes until the e tract has been reduced to the re uired volume as s ecified in the table belo . f the e tract volume a ears to sto dro ing, the concentration must be sto ed and the volume at hich it as sto ed recorded.

Water Content in Sample	**Concentrated Final Volume**
g	m
8 g	8 m
8 g	m
10 g	10 m

Note: Slowly concentrating extracts, in 1-mL increments, is necessary to prevent excessive concentration and the loss of neutral compounds (methyl and ethyl FOSEs and FOSAs) and other highly volatile compounds. The extract must be concentrated to remove the methanol as excess methanol during SPE clean-up results in poor recovery of C13 and C14 carboxylic acids and C10 and C12 sulfonates.

11.3.10 Add 40 - 0 m of reagent ater to the e tract and vorte . Chec that the is 6. 0. and adjust as necessary ith 0 formic acid (Section .1.13.4) or 30 ammonium hydro ide (or ith formic acid Section .1.13.3 and 3 a ueous ammonium hydro ide Section .1.6.2). The e tracts are ready for SPE and cleanu (Section 12.0).

11.4. Tissue Sam le Processing

Prior to rocessing tissue sam les, the laboratory must determine the e act tissue to be analy ed. Common re uests for analysis of fish tissue include hole fish ith the s in on, hole fish ith the s in removed, edible fish fillets (filleted in the field or by the laboratory), s ecific organs, and other ortions. Once the a ro riate tissue has been determined, the sam les must be re ared and homogeni ed.

f the laboratory must dissect the hole fish to obtain the a ro riate tissue for analysis, cover the benchto ith clean aluminum foil and use clean rocessing e ui ment (nives, scal els, t ee ers) to dissect each sam le to revent cross-contamination. Sam les should be handled in a semi-tha ed state for com ositing and or homogeni ation. All tissue com rising a sam le is collected in a stainless-steel bo l during grinding, then mi ed using a stainless-steel s oon. omogeni ed sam les must be stored in clean DPE containers and stored fro en for subse uent use.

f using a grinder, after the entire sam le has been rocessed, mi the ground tissue ith a s oon, transfer bac to the grinder, and re eat the grinding at least t o more times until the homogeni e tissue has a consistent te ture and color.

11.4.1 or each sam le, eigh a 2-g ali uot of homogeni ed tissue into a 1 -m oly ro ylene centrifuge tube. eseal the container ith the remaining homogeni ed ortion of the sam le and return it to fro en storage in the event that it needs to be used for reanalysis.

Note: The default sample weight for tissue is 2 g wet weight; however, a 1-g sample may be used. Higher sample weights are not recommended for this method.

11.4.2 Pre are the batch C sam les using 2 g of reference tissue matri (Section .2.3) for the method blan and t o OP s. S i e one OP sam le ith native standard solution (Section .3.3) at 2 the O (OP). This ali uot ill serve to verify the O . S i e the other OP sam le at the concentration of the mid-level calibration oint. This ali uot ill serve as the traditional OP .

Note: If matrix spikes are required for a specific project, spike the field sample aliquots designated as MS/MSD samples with native standard solution (Section 7.3.3) at the concentration 3 to 5 times the background concentration determined during screening of the unspiked sample. If screening was not performed, then spike those samples at the concentration of the mid-level calibration point.

11.4.3 S i e an ali uot of E S solution (Section .3.1) directly into each field and C sam le. orte and allo to e uilibrate for at least 30 minutes.

11.4.4 Add 10 m of 0.0 M O in methanol (Section .1.8) to each sam le. orte to dis erse the tissue then lace tubes on a variable s eed mi ing table to e tract for at least 16 hours. Centrifuge at 2800 r m for 10 minutes and collect the su ernatant in a 0-m oly ro ylene centrifuge tube.

11.4.5 Add 10 m of acetonitrile to remaining tissue in the 1 -m centrifuge tube, vorte to mi and dis erse the tissue. Sonicate for 30 minutes. Centrifuge at 2800 r m for 10 minutes and collect the su ernatant, adding it to the 0-m centrifuge tube containing the initial e tract.

11.4.6 Add m of 0.0 M O in methanol (Section .1.8) to the remaining sam le in each centrifuge tube. orte to dis erse the tissue and hand mi briefly. Centrifuge at 2800 r m for 10 minutes and collect the su ernatant, adding it to the 0-m centrifuge tube containing the first t o e tracts.

11.4.7 Using a 10-mg scoo , add 10 mg of carbon (Section .1.1) to the combined e tract, mi by occasional hand sha ing over a eriod of no more than five minutes and then centrifuge at 2800 r m for 10 minutes. mmediately decant the e tract into a 60-m glass eva oration or concentrator tube.

11.4.8 Add 1 m of reagent ater to each eva oration concentrator tube, set the eva orator concentrator to C ith a N_2 flo of 1.2 min and concentrate the e tract to 2. m (only 1 m of the methanol should remain).

11.4.9 Add reagent ater to each eva oration concentrator tube to dilute the e tracts to 0 m . Chec that the 6. 0. and adjust as needed ith 0 formic acid (Section .1.13.4)

or ammonium hydro ide (or ith formic acid Section .1.13.3 and 3 a ueous ammonium hydro ide .1.6.2). The e tracts are ready for SPE and cleanu (Section 12.0).

12.0 Extraction, Cleanup, and Concentration

All matrices (including batch C) must undergo SPE and carbon cleanu to remove interferences (Section 12.1). Sam le elution as ell as any further e tract treatment is matri s ecific and may be found in Sections 12.2 through 12.4.

Note: Carbon cleanup is required. Carbon cleanup may remove analytes if the sample has a very low organic carbon content (this is unusual for non-drinking water environmental samples). This will be apparent if the isotope dilution standard recoveries are significantly higher on the reanalysis. If the laboratory can demonstrate that the carbon cleanup is detrimental to the sample analysis (by comparing results when skipping the carbon cleanup during reanalysis), then the carbon cleanup may be skipped for that specific sample.

12.1 All sam le matrices

12.1.1 Pac clean silani ed glass ool to half the height of the WA SPE cartridge barrel (Section 6. .1).

12.1.2 Set u the vacuum manifold ith one WA SPE cartridge lus a reservoir and reservoir ada tor for each cartridge for each sam le and C ali uot.

12.1.3 Pre-condition the cartridges by ashing them ith 1 m of 1 methanolic ammonium hydro ide (Section .1. .2) follo ed by m of 0.3M formic acid (Section .1.13.2) (do not use the vacuum for this ste). Do not allo the WA SPE to go dry. Discard the ash solvents.

12.1.4 Pour the sam le into the reservoir (do not use a i ette), ta ing care to avoid s lashing hile loading. Adjust the vacuum and ass the sam le through the cartridge at m min. etain the em ty sam le bottle and allo it to air dry for later rinsing (Section 12.2.2). Discard eluate.

Note: For aqueous samples, in the event the SPE cartridge clogs during sample loading, place a second pre-conditioned cartridge and continue loading the remaining sample aliquot using the same reservoir. Proceed to Section 12.1.5.

12.1.5 inse the alls of the reservoir ith m reagent ater (t ice) follo ed by m of 1 1 0.1M formic acid methanol (Section .1.13.) and ass those rinses through the cartridge using vacuum. Dry the cartridge by ulling air through for 1 seconds. Discard the rinse solution. Continue to the elution and concentration ste s based on the matri (Section 12.2 A ueous, Section 12.3 Solids and Section 12.4 Tissue).

12.2 Elution and E tract Concentration of A ueous Sam les

Note: If two cartridges were used, perform Sections 12.2.1 through 12.2.3 with each cartridge. Filter the eluates through a 25-mm, 0.2-µm syringe filter. Combine both sets of filtered eluates into a clean tube, add the NIS solution, and vortex to mix. Transfer 350 µL of the filtered extract into a 1-mL polypropylene microvial and mark the level. Add another

350-µL portion and using a gentle stream of nitrogen (water bath at 40 ºC), concentrate to the 350-µL mark and submit for LC-MS/MS analysis. This concentration step is only applicable to situations where two SPE cartridges were eluted, each with 5 mL of elution solvent.

12.2.1 Place clean collection tubes (13 100 mm oly ro ylene) inside the manifold, ensuring that the e tract delivery needles do not touch the alls of the tubes. DO NOT add N S to these collection tubes.

12.2.2 inse the inside of the sam le bottle ith m of 1 methanolic ammonium hydro ide (Section .1. .2), then, using a glass i ette, transfer the rinse to the SPE reservoir, ashing the alls of the reservoir. Use vacuum to ull the elution solvent through the cartridge and into the collection tubes.

Note: Air dry the empty sample bottle after the rinse is transferred. Weigh the empty bottle with the cap on and subtract from the weight with the sample determined in Section 11.2.2.

12.2.3 Add 2 of concentrated acetic acid to each sam le eluted in the collection tubes and vorte to mi . Add 10 mg of carbon (Section .1.1) to each sam le and batch C e tract, using a 10-mg scoo . and-sha e occasionally for no more than minutes. t is im ortant to minimi e the time the sam le e tract is in contact ith the carbon. mmediately vorte (30 seconds) and centrifuge at 2800 r m for 10 minutes.

12.2.4 Add N S solution (Section .3.2) to a clean collection tube. Place a syringe filter (2 -mm filter, 0.2- m nylon membrane) on a -m oly ro ylene syringe. Ta e the lunger out and carefully decant the sam le su ernatant into the syringe barrel. e lace the lunger and filter the entire e tract into the ne collection tube containing the N S. orte to mi and transfer a ortion of the e tract into a 1-m oly ro ylene microvial for C-MS MS analysis. Ca the collection tube containing the remaining e tract and store at 0 - 4 C.

12.3 Elution and E tract Concentration of Solid Sam les

12.3.1 Add N S solution (Section .3.2) to a clean collection tube (13 100 mm oly ro ylene) for each sam le and C ali uot and lace them into the manifold rac , ensuring the e tract delivery needles are not touching the alls of the tubes.

12.3.2 inse the inside of the eva oration concentrator tube using m of 1 methanolic ammonium hydro ide (Section .1. .2), then, using a glass i ette, transfer the rinse to the reservoir, ashing the alls of the reservoir. Use the vacuum to ull the elution solvent through the cartridge and into the collection tubes.

12.3.3 Add 2 of concentrated acetic acid to each sam le e tract in its collection tube and s irl to mi . Place a syringe filter (2 -mm filter, 0.2- m nylon membrane) on a m oly ro ylene syringe. Ta e the lunger out and carefully decant 1 m of sam le e tract into the syringe barrel. e lace the lunger and filter into a 1-m oly ro ylene microvial for C-MS MS analysis. Ca the collection tube containing the remaining e tract and store at 0 - 4 C.

12.4 Elution and E tract Concentration of Tissue Sam les

12.4.1 Add N S solution (Section .3.2) to clean collection tubes (13 100 mm, oly ro ylene) for each sam le and C ali uot. Place the tubes into the manifold rac and ensure the e tract delivery needles are not touching the alls of the tubes.

12.4.2 inse the inside of the eva oration concentrator tube using m of 1 methanolic ammonium hydro ide (Section .1. .2), then, using a glass i ette, transfer the rinse to the reservoir, ashing the alls of the reservoir. Use the vacuum to ull the elution solvent through the cartridge and into the collection tubes.

12.4.3 Add 2 of concentrated acetic acid to each sam le e tract. Place a syringe filter (2 - mm filter, 0.2- m nylon membrane) on a m oly ro ylene syringe. Ta e the lunger out and carefully decant an ali uot (1 m) of the sam le e tract into the syringe barrel. e lace the lunger and filter into a 1-m oly ro ylene microvial for C-MS MS analysis. Ca the collection tube containing the remaining e tract and store at 0 - 4 C.

13.0 Instrumental Analysis

Analysis of sam le e tracts for P AS by C-MS MS is erformed on an ultrahigh erformance li uid chromatogra h cou led to a tri le uadru ole mass s ectrometer, running manufacturer s soft are. The mass s ectrometer is run ith unit mass resolution in the multi le reaction monitoring (M M) mode.

13.1 Perform mass calibration (Section 10.1), establish the o erating conditions (Section 10.2), and erform an initial calibration (Section 10.3) rior to analy ing sam les. f tissue sam les are to be analy ed during the analytical shift, re eat the TDCA interference chec in Section 10.3. before analy ing any field sam les.

13.2 Only after all erformance criteria are met may blan s, MD s, P s OP s, and sam les be analy ed.

13.3 After a successful initial calibration has been com leted, the analytical se uence for a batch of sam les analy ed during the same time eriod is as follo s. The volume injected for sam les and Cs must be identical to the volume used for calibration (Section 10.3). Standards and sam le e tracts must be brought to room tem erature and vorte ed rior to ali uoting into an instrument vial in order to ensure homogeneity of the e tract.

1. nstrument lan
2. nstrument Sensitivity Chec (see Section 10.3.3.1)
3. Calibration erification Standard
4. ualitative dentification Standards
. nstrument lan
6. Method lan
. o -level OP (OP)
8. OP
. TDCA standard (only if tissue sam les are being analy ed)
10. Sam les (10 or fe er)
11. Calibration erification Standard
12. nstrument lan
13. Sam les (10 or fe er)
14. Calibration erification Standard
1 . nstrument lan

If the results are acceptable, the closing calibration verification solution (#14 above) may be used as the opening solution for the next analytical sequence.

13.4 If the response exceeds the calibration range for any sample, extracts are diluted as per Section 15.3 to bring all target responses within the calibration range.

Note: If the analytes that exceed the calibration range in the original analysis are known to not be of concern for the specific project (e.g., are not listed in a discharge permit), then the laboratory may consult with the client regarding the possibility of reporting that sample from the undiluted analysis.

14.0 Performance Tests during Routine Operations

The following performance tests must be successfully completed as part of each routine instrumental analysis shift described in Section 13.3 above.

14.1 MS resolution – A mass calibration must be performed prior to analysis of the calibration curve. LC-MS/MS system performance is checked by performing an MS resolution verification after the mass calibration. MS resolution must be verified prior to any samples or QC as per Section 10.1. If the requirements in Section 10.1 cannot be met, the problem must be corrected before analyses can proceed. If any of the samples in the previous shift may be affected by poor mass resolution, the extracts of those samples must be re-analyzed.

14.2 Instrument sensitivity check

The signal-to-noise ratio of the ISC standard (Section 7.3.4) must be greater than or equal to 3:1. If the requirements cannot be met, the problem must be corrected before analyses can proceed.

Note: *An interim limit of 70-130% for 90% of the native and isotopically labeled compounds should be used, with the other recoveries achieving 50-150%.*

14.3 Calibration verification (CV)

After a passing MS resolution (Section 14.1) and a successful initial calibration (Section 10.3.3.3) is achieved, prior to the analysis of any samples, analyze a mid-level calibration standard (Section 7.3.4).

14.3.1 The calibration is verified by analyzing a CV standard at the beginning of each analytical sequence, every ten samples or less, and at the end of the analytical sequence.

14.3.2 Calculate concentration for each native and isotopically labeled compound in the CV using the equation in Section 15.2.

14.3.3 The recovery of native and isotopically labeled compounds for the CVs must be within 70 - 130%.

14.3.4 If the CV criterion in Section 14.3.3 is not met, recalibrate the LC-MS/MS instrument according to Section 10.3.

14.4 etention times and resolution

14.4.1 or all method analytes ith e act corres onding isoto ically labeled analogs, method analytes must elute ithin 0.1 minutes of the associated E S.

14.4.2 The retention times of each native and isoto ically labeled com ound must be ithin 0.4 minutes of the CA or C used to establish the T indo s for the sam les and batch C.

14.5 Ongoing recision and recovery (OP)

14.5.1 After verification, analy e the e tract of the OP (Sections 12.2.4, 12.3.3, and 12.4.3) rior to analysis of sam les from the same batch to ensure the analytical rocess is under control.

14.5.2 Com ute the ercent recovery of the native com ounds by the a ro riate uantification method de ending on the com ound (Section 10.3). Com ute the ercent recovery of each isoto ically labeled com ound by the non-e tracted internal standard method (Sections 1.2 and 10.3).

$$Recovery\ (\%) = \frac{Concentration\ found\ (ng/mL)}{Concentration\ spiked\ (ng/mL)}\ x\ 100$$

14.5.3 or the native com ounds and isoto ically labeled com ounds, com are the recovery to the OP limits given in Table . f all com ounds meet the acce tance criteria, system erformance is acce table, and analysis of blan s and sam les may roceed. f, ho ever, any individual concentration falls outside of the given range, the e traction concentration rocesses are not being erformed ro erly for that com ound. n this event, correct the roblem, re- re are, e tract, and clean u the sam le batch and re eat the ongoing recision and recovery test.

14.5.4 f desired, add results that ass the s ecifications in Section 14. .3 to initial and revious ongoing data for each com ound in each matri . U date C charts to form a gra hic re resentation of continued laboratory erformance. Develo a statement of laboratory accuracy for each com ound in each matri ty e by calculating the average ercent recovery ( ) and the standard deviation of ercent recovery (S). E ress the accuracy as a recovery interval from - 2S to 2S . or e am le, if and S , the accuracy is 8 to 10 .

14.6 nstrument blan At the beginning of the analytical se uence and after the analysis of high concentration sam les (e.g., highest calibration standard, C), analy e an instrument blan to ensure no instrument contamination has occurred.

14.7 Method blan After the analysis of the solvent blan and rior to the analysis of sam les, analy e a method blan (Section .).

14.8 A ualitative identification standard (Section .3.) containing all available isomers (branched and linear) is analy ed once daily at the beginning of the analytical se uence, to confirm the retention time of each linear and no n branched isomer or isomer grou .

14.9 nstrument sensitivity (o tional)

This ste is recommended as a follo -u ste if the SC does not meet criteria. Com are the N S ea areas from the C and field sam les to the average area of the corres onding N S on the calibration standards to chec for ossible bad injections of N S solution or loss of instrument sensitivity. The C and field sam le N S areas should be ithin 0 200 of that in the standards. f the areas are lo for all the sam les and C in the batch, it suggests a loss of instrument sensitivity, hile lo areas on only some C or field sam les suggests a ossible bad injection.

15.0 Data Analysis and Calculations

15.1 ualitative determination and ea identification

A native or isoto ically labeled com ound is identified in a standard, blan , sam le, or C sam le hen all of the criteria in Sections 1 .1.1 through 1 .1. are met.

15.1.1 Pea res onses must be at least three times the bac ground noise level (S N 3 1). f the S N ratio is not met due to high bac ground noise, the laboratory must correct the issue (e.g., erform instrument troubleshooting to chec and if needed, re lace, the transfer line, column, detector, liner, filament, etc.). f the S N ratio is not met but the bac ground is lo , then the analyte is to be considered a non-detect.

15.1.2 Target analyte, E S analyte, and N S analyte Ts must fall ithin 0.4 minutes of the redicted retention times from the mid oint standard of the CA or initial daily C , hichever as used to establish the T indo osition for the analytical batch. The retention time indo used must be of sufficient idth to detect earlier-eluting branched isomers. or all method analytes ith e act corres onding isoto ically labeled analogs, method analytes must elute ithin 0.1 minutes of the associated E S.

15.1.3 The laboratory must follo the identification re uirements s ecified by the client for the roject. n the event there are no roject-s ecific re uirements, the follo ing general re uirements a ly. or concentrations at or above the method O , the total (branched and linear isomer) uantification ion res onse to the total (branched and linear isomer) confirmation ion res onse ratio must fall ithin 0 of the ratio observed in the mid-oint initial calibration standard. f roject-s ecific re uirements involve re orting sam le concentrations belo the O or M , the res onse ratio must also fall ithin 0 of the ratio observed in the initial daily C .

The res onse of all isomers in the uantitative standards should be used to define ratio. n sam les, the total res onse should include only the branched isomer ea s that have been identified in either the uantitative or ualitative standard (see Section .3 regarding records of traceability of all standards). f standards (either uantitative or ualitative) are not available for urchase, only the linear isomer can be identified and uantitated in sam les. The ratio re uirement does not a ly for P A, P PeA, NMe OSE, NEt OSE, P MPA, and P M A because suitable (not detectable or inade uate S N) secondary transitions are unavailable.

15.1.4 f the field sam le result does not all meet the criteria stated in Sections 1 .1.2 through 1 .1.3, and all sam le re aration avenues (e.g., e tract cleanu , sam le dilution, etc.) have been e hausted, the result may only be re orted ith a data ualifier alerting the data user

that the result could not be confirmed because it did not meet the method-re uired criteria and therefore should be considered an estimated value. f the criteria listed above are not met for the standards, the laboratory must sto analysis of sam les and correct the issue.

15.2 uantitative determination

Concentrations of the target analytes are determined ith res ect to the e tracted internal standard (E S) hich is added to the sam le rior to e traction. The E S is uantitated ith res ect to a non-e tracted internal standard (N S), as sho n in Table 2, using the res onse ratios or res onse factors from the most recent multi-level initial calibration (Section 10.3). Other e uations may be used if the laboratory demonstrates that those e uations roduce the same numerical result as roduced by the e uations belo .

or the native analytes

$$Concentration\ (ng/L\ or\ ng/g) = \frac{Area_n\ M_l}{Area_l(\overline{RR}\ or\ \overline{RF})} \times \frac{1}{W_S}$$

where:

$Area_n$	The measured area of the 1 m for the native (unlabeled) P AS
$Area_l$	The measured area at the 1 m for the isoto ically labeled P AS (E S). *See note below.*
M_l	The mass of the isoto ically labeled com ound added (ng)
$\overline{RR}$	Average res onse ratio used to uantify target com ounds by the isoto e dilution method
$\overline{RF}$	Average res onse factor used to uantify target com ounds by the e tracted internal standard method
W_S	Sam le volume ( ) or eight (g)

Note: For better accuracy, PFTrDA is quantitated using the average of the areas of labeled compounds $^{13}C_2$-PFTeDA and $^{13}C_2$-PFDoA.

And for the E S analytes

$$Concentration\ (ng/L\ or\ ng/g) = \frac{Area_l\ M_{nis}}{Area_{nis}\overline{RF_s}} \times \frac{1}{W_S}$$

where:

$Area_l$	The measured area at the 1 m for the isoto ically labeled P AS (E S)
$Area_{nis}$	The measured area of the 1 m for the non-e tracted internal standard (N S)
M_{nis}	The mass of the added non-e tracted internal standard (N S) com ound (ng)
W_S	Sam le volume ( ) or eight (g)
$\overline{RF_s}$	Average res onse factor used to uantify the isoto ically labeled com ound by the non-e tracted internal standard method

esults for native com ounds are recovery corrected by the method of uantification. E tracted internal standard (E S) recoveries are determined similarly against the non-e tracted internal standard (N S) and are used as general indicators of overall analytical uality.

The instrument measures the target analytes as either their anions or neutral forms. **The default approach for Clean Water Act uses of the method is to report the analytes in their acid or neutral forms,** using the follo ing e uation to convert the concentrations

$$C_{Acid} = C_{Anion} \times \frac{MW_{Acid}}{MW_{Anion}}$$

where:

C_{Anion}	The analyte concentration in anion form
MW_{Acid}	The molecular eight of the acid form
MW_{Anion}	The molecular eight of the anion form

15.3 Sam le dilutions

15.3.1 f the 1 area for any com ound e ceeds the calibration range of the system, dilute a subsam le of the sam le e tract ith 0.1 acetic acid (Section .1.2) by a factor no greater than 10 adjust the amount of the N S in the diluted e tract, then analy e the diluted e tract using the ercent recovery of the E S from the original analysis. f the com ound cannot be measured reliably by isoto e dilution, dilute and analy e a ueous sam le, or analy e a smaller ali uot of soil, biosolid, sediment, or tissue sam le. Adjust the com ound concentrations, detection limits, and minimum levels to account for the dilution.

15.3.2 f the recovery of any isoto ically labeled com ound is outside of the acce tance limits (Table), a diluted a ueous sam le or smaller ali uot (for solids and tissue) must be analy ed (Section 1 .3.1). f the recovery of any isoto ically labeled com ound in the diluted sam le is outside of the normal range, the method does not a ly to the sam le being analy ed and the result may not be re orted or used for ermitting or regulatory com liance ur oses. n this case, an alternative column could be em loyed to resolve the interference. f all cleanu rocedures in this method and an alternative column have been em loyed and isoto ically labeled com ound recovery remains outside of the normal range, e traction and or cleanu rocedures that are beyond this sco e of this method ill be re uired to analy e the sam le.

15.4 e orting of analytical results (acid neutral forms)

The data re orting ractices described here are focused on NPDES monitoring needs and may not be relevant to other uses of the method. or analytes re orted in their acid form, use the e uations in Section 1 .2 and the analyte names Table 1. or analytes re orted in their anion form, see Table 8 for the a ro riate names and CAS egistry Numbers.

15.4.1 e ort results for a ueous sam les in ng . e ort results for solid sam les in ng g, on a dry- eight basis, and re ort the ercent solids for each sam le se arately. e ort results for tissue sam les in ng g, on a et- eight basis. Other units may be used if re uired in a ermit or for a roject. e ort all C data ith the sam le results.

15.4.2 e orting level

Unless s ecified other ise by a regulatory authority or in a discharge ermit, results for analytes that meet the identification criteria are re orted do n to the concentration of the M established by the laboratory through calibration of the instrument (see the glossary for the derivation of the M). EPA considers the terms re orting limit, uantitation limit, limit of uantitation, and minimum level to be synonymous.

15.4.2.1 e ort a result for each analyte in each field sam le or C standard at or above the M to 3 significant figures. e ort a result for each analyte found in each field sam le or C standard belo the M as M , here M is the

concentration of the analyte at the ML, or as required by the regulatory/control authority or permit.

15.4.2.2 Report a result for each analyte in a blank at or above the MDL to 2 significant figures. Report a result for each analyte found in a blank below the MDL as "<MDL," where MDL is the concentration of the analyte at the MDL, or as required by the regulatory/control authority or permit.

15.4.2.3 Report a result for an analyte found in a sample or extract that has been diluted at the least dilute level at which the area at the quantitation m/z is within the calibration range (e.g., above the ML for the analyte and below the highest calibration standard) and with isotopically labeled compound recoveries within their respective QC acceptance criteria. This may require reporting results for some analytes from different analyses.

15.4.2.4 Report recoveries of all associated EIS compounds for all field samples and QC standards.

15.4.3 Results from tests performed with an analytical system that is not in control (i.e., that does not meet acceptance criteria for any QC tests in this method) must be documented and reported (e.g., as a qualifier on results), unless the failure is not required to be reported as determined by the regulatory/control authority. Results associated with a QC failure cannot be used to demonstrate regulatory compliance. QC failures do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a reanalysis of the sample, the regulatory/control authority should be consulted for disposition.

16.0 Method Performance

Routine method performance is validated through analysis of matrix-specific reference samples, including spikes and certified reference materials. Ongoing method performance is monitored through QC samples analyzed alongside samples. The parameters monitored include percent recovery of isotopically labeled compounds, blank concentrations, and native compound recoveries.

This method is being validated, and performance specifications will be developed using data from DOD's interlaboratory validation study (Reference 10). A summary of the single-laboratory performance is presented in Tables 5, 9, and 10.

17.0 Pollution Prevention

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When wastes cannot be reduced feasibly at the source, EPA recommends recycling as the next best option.

17.2 The compounds in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

17.3 or information about ollution revention that may be a lied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction* (eference).

18.0 Waste Management

18.1 The laboratory is res onsible for com lying ith all ederal, State, and local regulations governing aste management, articularly the ha ardous aste identification rules and land dis osal restrictions, and to rotect the air, ater, and land by minimi ing and controlling all releases from fume hoods and bench o erations. Com liance is also re uired ith any se age discharge ermits and regulations. An overvie of re uirements can be found in *Environmental Management Guide for Small Laboratories* (eference 8).

18.2 Sam les at 2 or 12, are ha ardous and must be handled and dis osed of as ha ardous aste or neutrali ed and dis osed of in accordance ith all federal, state, and local regulations. t is the laboratory s res onsibility to com ly ith all federal, state, and local regulations governing aste management, articularly the ha ardous aste identification rules and land dis osal restrictions.

18.3 or further information on aste management, consult The Waste Management Manual for aboratory Personnel and ess is etter- aboratory Chemical Management for Waste eduction, (eference).

19.0 References

1. Wor ing ith Carcinogens, De artment of ealth, Education, Welfare, Public ealth Service, Centers for Disease Control, N OS , Publication -206, August 1 , NT S P - 2 2 6.

2. OS A Safety and ealth Standards, eneral ndustry, OS A 2206, 2 C 1 10.

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4. Standard Methods for the E amination of Water and Waste ater, 18th edition and later revisions, American Public ealth Association, 101 1 th St, NW, Washington, DC 2000 , 1-3 Section 10 0 (Safety), 1 2.

. Standard Practice for Sam ling Water, ASTM Annual oo of Standards, ASTM, 1 16 ace Street, Philadel hia, PA 1 103-118 , 1 80.

6. andboo of Analytical uality Control in Water and Waste ater aboratories, USEPA EMS , Cincinnati, O 4 268, EPA 600 4- -01 , A ril 1 .

. ess is etter aboratory Chemical Management for Waste eduction, American Chemical Society, 1 3. Available from the American Chemical Society s De artment of overnment elations and Science Policy, 11 16th Street NW, Washington, DC 20036.

8. Environmental Management uide for Small aboratories, USEPA, Small usiness Division, Washington DC, EPA 233- -00-001, May 2000.

. The Waste Management Manual for aboratory Personnel, American Chemical Society, 1 0. Available from the American Chemical Society s De artment of overnment elations and Science Policy, 11 16th Street NW, Washington, DC 20036.

10. *DOD single- laboratory study reference will be added here.*

11. *DOD interlaboratory study reference will be added here.*

12. DoD SM (US De artment of Defense uality Systems Manual for Environmental aboratories, version .3, 201)

13. Woudneh, Million ., harat Chandramouli, Coreen amilton, ichard race, 201 , Effects of Sam le Storage on the uantitative Determination of 2 P AS Observation of Analyte nterconversions during Storage , Environmental Science and Technology 3(21) 12 6-12 8 .

20.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 1. Names, Abbreviations, and CAS Registry Numbers for Target PFAS, Extracted Internal Standards and Non-extracted Internal Standards[1]

Target Analyte Name	Abbreviation	CAS Number
Perfluoroalkyl carboxylic acids		
Perfluorobutanoic acid	P A	3 -22-4
Perfluoro entanoic acid	P PeA	2 06- 0-3
Perfluorohe anoic acid	P A	30 -24-4
Perfluorohe tanoic acid	P A	3 -8 -
Perfluorooctanoic acid	P OA	33 -6 -1
Perfluorononanoic acid	P NA	3 - -1
Perfluorodecanoic acid	P DA	33 - 6-2
Perfluoroundecanoic acid	P UnA	20 8- 4-8
Perfluorododecanoic acid	P DoA	30 - -1
Perfluorotridecanoic acid	P TrDA	262 - 4-8
Perfluorotetradecanoic acid	P TeDA	3 6-06-
Perfluoroalkyl sulfonic acids		
Acid Form		
Perfluorobutanesulfonic acid	P S	3 - 3-
Perfluoro entansulfonic acid	P PeS	2 06- 1-4
Perfluorohe anesulfonic acid	P S	3 -46-4
Perfluorohe tanesulfonic acid	P S	3 - 2-8
Perfluorooctanesulfonic acid	P OS	1 63-23-1
Perfluorononanesulfonic acid	P NS	682 -12-1
Perfluorodecanesulfonic acid	P DS	33 - -3
Perfluorododecanesulfonic acid	P DoS	80-3 -
Fluorotelomer sulfonic acids		
1*H*,1*H*, 2*H*, 2*H*-Perfluorohe ane sulfonic acid	4 2 TS	124- 2-4
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6 2 TS	2 61 - -2
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8 2 TS	3 108-34-4
Perfluorooctane sulfonamides		
Perfluorooctanesulfonamide	P OSA	4- 1-6
N-methyl erfluorooctanesulfonamide	NMe OSA	31 06-32-8
N-ethyl erfluorooctanesulfonamide	NEt OSA	41 1- 0-2
Perfluorooctane sulfonamidoacetic acids		
N-methyl erfluorooctanesulfonamidoacetic acid	NMe OSAA	23 -31-
N-ethyl erfluorooctanesulfonamidoacetic acid	NEt OSAA	2 1- 0-6
Perfluorooctane sulfonamide ethanols		
N-methyl erfluorooctanesulfonamidoethanol	NMe OSE	24448-0 -
N-ethyl erfluorooctanesulfonamidoethanol	NEt OSE	16 1- -2
Per- and Polyfluoroether carboxylic acids		
e afluoro ro ylene o ide dimer acid	PO-DA	132 2-13-6
4,8-Dio a-3*H*- erfluorononanoic acid	ADONA	1 00 -14-4
Perfluoro-3-metho y ro anoic acid	P MPA	3 - 3-1
Perfluoro-4-metho ybutanoic acid	P M A	8630 0-8 -
Nonafluoro-3,6-dio ahe tanoic acid	N D A	1 1 2- 8-6

Table 1. Names, Abbreviations, and CAS Registry Numbers for Target PFAS, Extracted Internal Standards and Non-extracted Internal Standards[1]

Target Analyte Name	Abbreviation	CAS Number
Ether sulfonic acids		
-Chlorohe adecafluoro-3-o anonane-1-sulfonic acid	Cl-P 3ONS	6426- 8-1
11-Chloroeicosafluoro-3-o aundecane-1-sulfonic acid	11Cl-P 3OUdS	630 1- 2-
Perfluoro(2-etho yethane)sulfonic acid	P EESA	113 0 -82-
Fluorotelomer carboxylic acids		
3-Perfluoro ro yl ro anoic acid	3 3 TCA	3 6-02-
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	3 TCA	1463 -4 -3
3-Perfluorohe tyl ro anoic acid	3 TCA	812- 0-4
EIS Compounds		
Perfluoro-n- $^{13}C_4$ butanoic acid	$^{13}C_4$-P A	NA
Perfluoro-n- ^{13}C entanoic acid	^{13}C -P PeA	
Perfluoro-n- 1,2,3,4,6-^{13}C he anoic acid	^{13}C -P A	
Perfluoro-n- 1,2,3,4-$^{13}C_4$ he tanoic acid	$^{13}C_4$-P A	
Perfluoro-n- $^{13}C_8$ octanoic acid	$^{13}C_8$-P OA	
Perfluoro-n- ^{13}C nonanoic acid	^{13}C -P NA	
Perfluoro-n- 1,2,3,4, ,6-$^{13}C_6$ decanoic acid	$^{13}C_6$-P DA	
Perfluoro-n- 1,2,3,4, ,6, -^{13}C undecanoic acid	^{13}C -P UnA	
Perfluoro-n- 1,2-$^{13}C_2$ dodecanoic acid	$^{13}C_2$-P DoA	
Perfluoro-n- 1,2-$^{13}C_2$ tetradecanoic acid	$^{13}C_2$-P TeDA	
Perfluoro-1- 2,3,4-$^{13}C_3$ butanesulfonic acid	$^{13}C_3$-P S	
Perfluoro-1- 1,2,3-$^{13}C_3$ he anesulfonic acid	$^{13}C_3$-P S	
Perfluoro-1- $^{13}C_8$ octanesulfonic acid	$^{13}C_8$-P OS	
Perfluoro-1- $^{13}C_8$ octanesulfonamide	$^{13}C_8$-P OSA	
N-methyl-d_3- erfluoro-1-octanesulfonamidoacetic acid	D_3-NMe OSAA	
N-ethyl-d - erfluoro-1-octanesulfonamidoacetic acid	D -NEt OSAA	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1- 1,2-$^{13}C_2$ he an sulfonic acid	$^{13}C_2$-4 2 TS	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1- 1,2-$^{13}C_2$ octanesulfonic acid	$^{13}C_2$-6 2 TS	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1- 1,2-$^{13}C_2$ decanesulfonic acid	$^{13}C_2$-8 2 TS	
Tetrafluoro-2-he tafluoro ro o y-$^{13}C_3$- ro anoic acid	$^{13}C_3$- PO-DA	
N-methyl-d - erfluorooctanesulfonamidoethanol	D -NMe OSE	
N-ethyl-d - erfluorooctanesulfonamidoethanol	D -NEt OSE	
N-ethyl-d - erfluoro-1-octanesulfonamide	D -NEt OSA	
N-methyl-d_3- erfluoro-1-octanesulfonamide	D_3-NMe OSA	
NIS Compounds		
Perfluoro-n- 2,3,4-$^{13}C_3$ butanoic acid	$^{13}C_3$-P A	NA
Perfluoro-n- 1,2,3,4-$^{13}C_4$ octanoic acid	$^{13}C_4$-P OA	
Perfluoro-n- 1,2-$^{13}C_2$ decanoic acid	$^{13}C_2$-P DA	
Perfluoro-n- 1,2,3,4-$^{13}C_4$ octanesulfonic acid	$^{13}C_4$-P OS	
Perfluoro-n- 1,2,3,4, -^{13}C nonanoic acid	^{13}C -P NA	
Perfluoro-n- 1,2-$^{13}C_2$ he anoic acid	$^{13}C_2$-P A	
Perfluoro-1-he ane $^{18}O_2$ sulfonic acid	$^{18}O_2$-P S	

[1] The target analyte names are for the acid and neutral forms of the analytes. See Table 8 for the names and CAS N of the corres onding anion forms, here a licable.

NA Not assigned a CAS N

Table 2. Analyte Ions Monitored, Extracted Internal Standard, and Non-extracted Internal Standard Used for Quantification

Abbreviation	Example Retention Time [1]	Parent Ion Mass	Quantification Ion Mass	Confirmation Ion Mass	Typical Ion Ratio	Quantification Reference Compound
Target Analytes						
P A	1. 6	212.8	168.	NA	NA	$^{13}C_4$-P A
P PeA	4.18	263.0	21 .0	68.	NA	^{13}C -P PeA
P A	4.81	313.0	26 .0	118.	13	^{13}C -P A
P A	.32	363.1	31 .0	16 .0	3.	$^{13}C_4$-P A
P OA	6.16	413.0	36 .0	16 .0	3.0	$^{13}C_8$-P OA
P NA	6.	463.0	41 .0	21 .0	4.	^{13}C -P NA
P DA	.4	12.	46 .0	21 .0	.	$^{13}C_6$-P DA
P UnA	.81	63.1	1 .0	26 .1	6.	^{13}C -P UnA
P DoA	8.13	613.1	6 .0	31 .0	10	$^{13}C_2$-P DoA
P TrDA[2]	8. 3	663.0	61 .0	168.	6.	avg.$^{13}C_2$-P TeDA and$^{13}C_2$-P DoA
P TeDA	8. 6	13.1	66 .0	168.	6.0	$^{13}C_2$-P TeDA
P S	4.	2 8.	.	8.8	2.1	$^{13}C_3$-P S
P PeS	.38	34 .1	.	8.	1.8	$^{13}C_3$-P S
P S	6.31	3 8.	8.	.	1.	$^{13}C_3$-P S
P S	.11	44 .0	.	8.8	1.	$^{13}C_8$-P OS
P OS	.	4 8.	.	8.8	2.3	$^{13}C_8$-P OS
P NS	. 2	48.8	.	8.8	1.	$^{13}C_8$-P OS
P DS	8.28	.0	.	8.8	1.	$^{13}C_8$-P OS
P DoS	.14	6 .1	.	8.8	1.	$^{13}C_8$-P OS
4 2 TS	4.6	32 .1	30 .0	80.	1.	$^{13}C_2$-4 2 TS
6 2 TS	.81	42 .1	40 .0	80.	1.	$^{13}C_2$-6 2 TS
8 2 TS	.28	2 .1	0 .0	80.8	3.0	$^{13}C_2$-8 2 TS
P OSA	8.41	4 8.1	.	4 8.0	4	$^{13}C_8$-P OSA
NMe OSA	. 0	11.	21 .0	16 .0	0.66	D_3-NMe OSA
NEt OSA	. 4	26.0	21 .0	16 .0	0.63	D -NEt OSA
NMe OSAA	. 1	0.1	41 .0	483.0	2.0	D_3-NMe OSAA
NEt OSAA	.6	84.2	41 .1	26.0	1.2	D -N-Et OSAA
NMe OSE	.	616.1	8.	NA	NA	D -NMe OSE
NEt OSE	.8	630.0	8.	NA	NA	D -NEt OSE
PO-DA	4.	284.	168.	184.	1.	$^{13}C_3$- PO-DA
ADONA	.	3 6.	2 0.	84.8	2.8	$^{13}C_3$- PO-DA
Cl-P 3ONS	.82	30.8	3 1.0	532.8→353.0	3.2	$^{13}C_3$- PO-DA
11Cl-P 3OUdS	8.62	630.	4 0.	632.9→452.9	3.0	$^{13}C_3$- PO-DA
3 3 TCA	3.8	241.0	1 .0	11 .0	1. 0	^{13}C -P PeA
3 TCA	.14	341.0	23 .1	21 .0	1.16	^{13}C -P A
3 TCA	6. 6	441.0	316.	336.	0.6	^{13}C -P A
P EESA	.08	314.8	134.	82.	.22	^{13}C -P A
P MPA	3.21	22 .0	84.	NA	NA	^{13}C -P PeA
P M A	4. 3	2 .0	8 .1	NA	NA	^{13}C -P PeA
N D A	4.84	2 .0	201.0	84.	1.46	^{13}C -P A
Extracted Internal Standards						
$^{13}C_4$-P A	1.	216.8	1 1.	NA		$^{13}C_3$-P A
^{13}C -P PeA	4.18	268.3	223.0	NA		$^{13}C_2$-P A
^{13}C -P A	4.80	318.0	2 3.0	120.3		$^{13}C_2$-P A
$^{13}C_4$-P A	.32	36 .1	322.0	NA		$^{13}C_2$-P A
$^{13}C_8$-P OA	6.16	421.1	3 6.0	NA		$^{13}C_4$-P OA

Table 2. Analyte Ions Monitored, Extracted Internal Standard, and Non-extracted Internal Standard Used for Quantification

Abbreviation	Example Retention Time [1]	Parent Ion Mass	Quantification Ion Mass	Confirmation Ion Mass	Typical Ion Ratio	Quantification Reference Compound
^{13}C -P NA	6.	4 2.1	42 .0	NA		^{13}C -P NA
$^{13}C_6$-P DA	.4	1 .1	4 4.1	NA		$^{13}C_2$-P DA
$^{13}C_7$-P UnA	.81	0.0	2 .1	NA		$^{13}C_2$-P DA
$^{13}C_2$-P DoA	8.13	61 .1	0.0	NA		$^{13}C_2$-P DA
$^{13}C_2$-P TeDA	8. 6	1 .2	6 0.0	NA		$^{13}C_2$-P DA
$^{13}C_3$-P S	4. 8	302.1	.	8.		$^{18}O_2$-P S
$^{13}C_3$-P S	6.30	402.1	.	8.8		$^{18}O_2$-P S
$^{13}C_8$-P OS	.	0 .1	8.	.		$^{13}C_4$-P OS
$^{13}C_2$-4 2 TS	4.6	32 .1	80.	30 .0		$^{18}O_2$-P S
$^{13}C_2$-6 2 TS	.82	42 .1	80.	40 .0		$^{18}O_2$-P S
$^{13}C_2$-8 2 TS	.28	2 .1	80.	0 .0		$^{18}O_2$-P S
$^{13}C_8$-P OSA	8.41	06.1	.8	NA		$^{13}C_4$-P OS
D_3-NMe OSA	. 0	1 .0	21 .0	NA		$^{13}C_4$-P OS
D -NEt OSA	. 4	31.1	21 .0	NA		$^{13}C_4$-P OS
D_3-NMe OSAA	. 1	3.2	41 .0	NA		$^{13}C_4$-P OS
D -NEt OSAA	.6	8 .2	41 .0	NA		$^{13}C_4$-P OS
D -NMe OSE	. 6	623.2	8.	NA		$^{13}C_4$-P OS
D -NEt OSE	.83	63 .2	8.	NA		$^{13}C_4$-P OS
$^{13}C_3$- PO-DA	4.	284.	168.	184.		$^{13}C_2$-P A
Non-Extracted Internal Standards						
$^{13}C_3$-P A	1.	216.0	1 2.0	NA		
$^{13}C_2$-P A	4.80	31 .1	2 0.0	11 .4		
$^{13}C_4$-P OA	6.16	41 .1	1 2.0	NA		
$^{13}C_5$-P NA	6.	468.0	423.0	NA		
$^{13}C_2$-P DA	.4	1 .1	4 0.1	NA		
$^{18}O_2$-P S	6.30	403.0	83.	NA		
$^{13}C_4$-P OS	.	02.8	.	8.		

[1] Times sho n are in decimal minute units. E am le retention times are based on the instrument o erating conditions and column s ecified in Section 10.2.

[2] or im roved accuracy, P TrDA is uantitated using the average areas of the labeled com ounds $^{13}C_2$-P TeDA and $^{13}C_2$-P DoA.

Table 3. Nominal Masses of Spike Added to Samples or Extracts

Analyte	Amount Added (ng)
Extracted Internal Standards	
$^{13}C_4$-P A	40
^{13}C -P PeA	20
^{13}C -P A	10
$^{13}C_4$-P A	10
$^{13}C_8$-P OA	10
^{13}C -P NA	
$^{13}C_6$-P DA	
^{13}C -P UnA	
$^{13}C_2$-P DoA	
$^{13}C_2$-P TeDA	
$^{13}C_3$-P S	10
$^{13}C_3$-P S	10
$^{13}C_8$-P OS	10
$^{13}C_2$-4 2 TS	20
$^{13}C_2$-6 2 TS	20
$^{13}C_2$-8 2 TS	20
$^{13}C_8$-P OSA	10
D_3-NMe OSA	10
D -NEt OSA	10
D_3-NMe OSAA	20
D -NEt OSAA	20
D -NMe OSE	100
D -NEt OSE	100
$^{13}C_3$- PO-DA	40
Non-extracted Internal Standards	
$^{13}C_3$-P A	20
$^{13}C_2$-P A	10
$^{13}C_4$-P OA	10
^{13}C -P NA	
$^{13}C_2$-P DA	
$^{18}O_2$-P S	10
$^{13}C_4$-P OS	10

Table 4. Calibration Solutions (ng/mL)

Compound	CS1 (LOQ)	CS2	CS3	CS4 (CV[1])	CS5	CS6	CS7[2]
Perfluoroalkyl carboxylic acids							
P A	0.8	2		10	20	0	2 0
P PeA	0.4	1	2.		10	2	12
P A	0.2	0.	1.2	2.		12.	62.
P A	0.2	0.	1.2	2.		12.	62.
P OA	0.2	0.	1.2	2.		12.	62.
P NA	0.2	0.	1.2	2.		12.	62.
P DA	0.2	0.	1.2	2.		12.	62.
P UnA	0.2	0.	1.2	2.		12.	62.
P DoA	0.2	0.	1.2	2.		12.	62.
P TrDA	0.2	0.	1.2	2.		12.	62.
P TeDA	0.2	0.	1.2	2.		12.	62.
Perfluoroalkyl sulfonic acids							
P S	0.2	0.	1.2	2.		12.	62.
P PeS	0.2	0.	1.2	2.		12.	62.
P S	0.2	0.	1.2	2.		12.	62.
P S	0.2	0.	1.2	2.		12.	62.
P OS	0.2	0.	1.2	2.		12.	62.
P NS	0.2	0.	1.2	2.		12.	62.
P DS	0.2	0.	1.2	2.		12.	62.
P DoS	0.2	0.	1.2	2.		12.	62.
Fluorotelomer sulfonic acids							
4 2 TS	0.8	2		10	20	0	NA
6 2 TS	0.8	2		10	20	0	NA
8 2 TS	0.8	2		10	20	0	NA
Perfluorooctane sulfonamides							
P OSA	0.2	0.	1.2	2.		12.	62.
NMe OSA	0.2	0.	1.2	2.		12.	62.
NEt OSA	0.2	0.	1.2	2.		12.	62.
Perfluorooctane sulfonamidoacetic acids							
NMe OSAA	0.2	0.	1.2	2.		12.	62.
NEt OSAA	0.2	0.	1.2	2.		12.	62.
Perfluorooctane sulfonamide ethanols							
NMe OSE	2		12.	2	0	12	62
NEt OSE	2		12.	2	0	12	62
Per- and polyfluoroether carboxylic acids							
PO-DA	0.8	2		10	20	0	2 0
ADONA	0.8	2		10	20	0	2 0
P MPA	0.4	1	2.		10	2	12
P M A	0.4	1	2.		10	2	12
N D A	0.4	1	2.		10	2	12
Ether sulfonic acids							
Cl-P 3ONS	0.8	2		10	20	0	2 0
11Cl-P 3OUdS	0.8	2		10	20	0	2 0
P EESA	0.4	1	2.		10	2	12

Table 4. Calibration Solutions (ng/mL)

Compound	CS1 (LOQ)	CS2	CS3	CS4 (CV[1])	CS5	CS6	CS7[2]
Fluorotelomer carboxylic acids							
3 3 TCA	1.0	2.	6.26	12.	2	62.4	312
3 TCA	.0	12.	31.3	62.	12	312	1 60
3 TCA	.0	12.	31.3	62.	12	312	1 60
Extracted Internal Standard (EIS) Analytes							
$^{13}C_4$-P A	10	10	10	10	10	10	10
^{13}C -P PeA							
^{13}C -P A	2.	2.	2.	2.	2.	2.	2.
$^{13}C_4$-P A	2.	2.	2.	2.	2.	2.	2.
$^{13}C_8$-P OA	2.	2.	2.	2.	2.	2.	2.
^{13}C -P NA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
$^{13}C_6$-P DA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
^{13}C -P UnA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
$^{13}C_2$-P DoA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
$^{13}C_2$-P TeDA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
$^{13}C_3$-P S	2.	2.	2.	2.	2.	2.	2.
$^{13}C_3$-P S	2.	2.	2.	2.	2.	2.	2.
$^{13}C_8$-P OS	2.	2.	2.	2.	2.	2.	2.
$^{13}C_2$-4 2 TS							
$^{13}C_2$-6 2 TS							
$^{13}C_2$-8 2 TS							
$^{13}C_8$-P OSA	2.	2.	2.	2.	2.	2.	2.
D_3-NMe OSA	2.	2.	2.	2.	2.	2.	2.
D -NEt OSA	2.	2.	2.	2.	2.	2.	2.
D_3-NMe OSAA							
D -NEt OSAA							
D -NMe OSE	2	2	2	2	2	2	2
D -NEt OSE	2	2	2	2	2	2	2
$^{13}C_3$- PO-DA	10	10	10	10	10	10	10
Non-extracted Internal Standard (NIS) Analytes							
$^{13}C_3$-P A							
$^{13}C_2$-P A	2.	2.	2.	2.	2.	2.	2.
$^{13}C_4$-P OA	2.	2.	2.	2.	2.	2.	2.
^{13}C -P NA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
$^{13}C_2$-P DA	1.2	1.2	1.2	1.2	1.2	1.2	1.2
$^{18}O_2$-P S	2.	2.	2.	2.	2.	2.	2.
$^{13}C_4$-P OS	2.	2.	2.	2.	2.	2.	2.

[1] This calibration oint is used as the calibration verification (C)

[2] A minimum of si contiguous calibrations standards are re uired for linear models and a minimum of seven calibration standards are re uired for second-order models.

Table 5. Single-Laboratory Validation Performance Summary for Target Compounds and Extracted Internal Standards

Compounds	Blank (ng/mL)	Aqueous Matrices[1]			Solid Matrices[1]			Tissue Matrices[1]		
		IPR Rec (%)	RSD (%)	OPR Rec (%)	IPR Rec (%)	RSD (%)	OPR Rec (%)	IPR Rec (%)	RSD (%)	OPR Rec (%)
Target Compounds										
P A	0.4	8 - 10	4.8	8 113		1.0	2 108	8 104	3.	0 110
P PeA	0.2	8 - 106	.	8 121	2 10	3.4	4 11	80 8	.0	6 114
P A	0.1	- 10	.1	8 111	3 101	2.2	8 10	2 110	10.2	0 111
P A	0.1	8 - 102	4.1	0 110	4 102	2.2	8 10	8 102	4.0	8 118
P OA	0.1	88 - 8	2.8	8 112	2 100	2.0	0 106	8 8	2.4	82 114
P NA	0.1	88 - 104	4.1	0 111	1 102	2.	88 112	8 110	6.3	8 11
P DA	0.1	82 - 11	8.3	2 11	103	1.	8 118	6 11	10.2	84 112
P UnA	0.1	83 - 8	4.2	8 112	1 10	4.0	2 111	83 102	.1	1 11
P DoA	0.1	8 - 111	1 .	84 123	3 120	12.1	88 11	83 10	.	141
P TrDA	0.1	80 - 111	8.1	2 11	1 112	.2	8 12	2 114	.3	106 133
P TeDA	0.1	88 - 103	4.1	8 116	4 104	2.	2 110	6 103	.4	1 111
P S	0.1	8 - 111	6.6	8 116	1 103	3.2	1 111	6 10	10.3	8 11
P PeS	0.1	8 - 11	6.	8 11	8 103	4.3	8 112	6	.4	8 112
P S	0.1	0 - 10	4.4	11	8 106	2.0	6 113	81 101	.3	1 123
P S	0.1	84 - 126	10.2	86 114	8 104	4.4	88 104	108	8.4	86 108
P OS	0.1	3 - 122	6.	1 120	108	3.4	4 11	8 112	3.2	124
P NS	0.1	64 - 141	18.8	86 123	8 111	3.0	6 11	6 88	.	8 114
P DS	0.1	- 121	11.	84 10	83 102	.2	84 10	82 4	3.6	8 110
P DoS	0.1	4 - 114	10.6	8 102	6	6.	100	3 6	6.	2 108
4 2 TS	0.4	6 - 123	12.0	1 11	8 100	0.	8 113	66 126	1 .6	0 103
6 2 TS	0.4	1 - 148	1 .	81 12	4 123	6.	60 166	10	.8	2 11
8 2 TS	0.4	8 - 10	6.1	124	10 128	3.8	104 12	66 148	1 .3	102 136
P OSA	0.1	0 - 10	4.4	1 122	2 106	3.4	4 114	2 116	.	6 121
NMe OSA	0.1	8 - 0	3.6	84 112	8 104	4.4	1 11	81 100	.	86 11
NEt OSA	0.1	-	.0	83 108	8 102	1.0	6 11	4 114	10.	0 12
NMe OSAA	0.1	82 - 11	8.2	81 120	1 10	4.0	0 113	8 136	10.4	3 11
NEt OSAA	0.1	- 120	10.3	8 124	102 108	1.6	8 11	3 11	18.3	0 11
NMe OSE	1	8 - 102	3.	2 11	8 103	1.3	4 112	1 2 2	30.3	118 344
NEt OSE	1	8 - 104	4.	1 118	104	1.	6 11	133	8.0	61 1
PO-DA	0.4	88 - 114	6.	84 118	83 10	.	80 120	3 100	.8	86 114
ADONA	0.4	- 106	.	11	8 6	3.2	6 124	82	3.8	86 132
P MPA	0.2	86 - 106	6.6	83 120	1 8	1.8	8 11	8 3	4.2	86 10
P M A	0.2	62 - 122	.2	81 11	88	2.6	8 120	4 104	8.4	84 11
N D A	0.2	44 - 14	16.3	6 138	3 103	16.2	8 136	4 86	13.8	6 11
Cl-P 3ONS	0.4	84 - 101	2 .4	80 120	84 100	4.4	131	6 8	8.	126
11Cl-P 3OUdS	0.4	80 -	4.	6 116	84 6	3.3	12	8 100	4.3	4 138
P EESA	0.2	80 - 104	4.4	8 11	80 3	3.8	8 10	68	.3	88 10
3 3 TCA	0.	84 - 103	.0	66 12	86 8	3.3	6 116	66 4	.0	41 126
3 TCA	2.	84 - 101	4.6	84 113	83 4	3.1	80 101	131	.	8 1
3 TCA	2.	8 - 103	.0	82 116	0 106	4.1	104	84 111	6.	13

Table 5. Single-Laboratory Validation Performance Summary for Target Compounds and Extracted Internal Standards

Compounds	Blank (ng/mL)	Aqueous Matrices[1]			Solid Matrices[1]			Tissue Matrices[1]		
		IPR Rec (%)	RSD (%)	OPR Rec (%)	IPR Rec (%)	RSD (%)	OPR Rec (%)	IPR Rec (%)	RSD (%)	OPR Rec (%)
Extracted Internal Standard (EIS)										
$^{13}C_4$-P A	N A	8 - 1	1.6	88 108	2	1.6	10	3	1.0	10
^{13}C -P PeA	N A	8 -	2.4	84 111	86 106	.3	80 110	8 108	6.0	8 103
^{13}C -P A	N A	8 - 2	1.	83 108	83 101	4.8	2 106	111	8.	88 8
$^{13}C_4$-P A	N A	8 - 100	6.2	83 106	8 102	4.1	0 100	88 3	1.3	80 102
$^{13}C_8$-P OA	N A	- 8	6.0	84 10	8 101	3.2	2 104	1 8	1.	86 102
^{13}C -P NA	N A	82 - 6	3.8	84 10	86 101	4.1	0 106	1 104	3.3	8 101
$^{13}C_6$-P DA	N A	81 - 8	4.	84 106	101	6.0	86 10	8 104	4.0	0 104
^{13}C -P UnA	N A	84 - 100	4.4	84 10	84 104	.4	1 116	84 118	8.4	88 10
$^{13}C_2$-P DoA	N A	61 - 103	12.	3 101	0 3	.1	3 106	12	6.8	0 108
$^{13}C_2$-P TeDA	N A	2 - 8	.4	4	83 88	1.	4 10	81 114	8.	10 110
$^{13}C_3$-P S	N A	8 - 4	2.0	88 110	10	1.8	6 10	8 114	6.	106
$^{13}C_3$-P S	N A	83 - 8	1.	8 103	2	1.4	2 106	2	1.4	1 103
$^{13}C_8$-P OS	N A	8 - 2	3.	86 110	8 10	4.	10	8 3	1.6	103
$^{13}C_2$-4 2 TS	N A	64 - 106	12.1	8 13	132 13	0.6	123 14	106 221	1 .6	1 2 1
$^{13}C_2$-6 2 TS	N A	3 - 102	2.2	6 14	118 12	2.3	104 138	8 13	10.8	11 14
$^{13}C_2$-8 2 TS	N A	- 10	2.	1 13	6 122	6.1	3 123	1 2	12.	304
$^{13}C_8$-P OSA	N A	60 - 10	14.2	10	6 86	.4	66 100	104 1 3	.4	88 120
D_3-NMe OSA	N A	- 8	10.8	3 84	4	.4	2 64	20 8	24.	3 34
D -NEt OSA	N A	4 - 1	12.	43 84	43 1	4.	18 8	30 6	1 .2	0 6
D_3-NMe OSAA	N A	63 - 11	14.	66 11	8 10	2.1	86 10	102 18	14.	144 1 6
D -NEt OSAA	N A	66 - 11	13.	63 11	8 104	1.3	8 10	1 8 216	4.	1 223
D -NMe OSE	N A	61 - 106	13.6	42	0 61	.1	3 6	3	11.6	0 8
D -NEt OSE	N A	63 - 108	13.2	44 0	46	.	32 2	8 33	30.0	0 33
$^{13}C_3$- PO-DA	N A	8 - 106	4.	88 121	8 108	2.4	83 12	8 106	4.	81 106

[1] The recovery limits are a lied to all sam les, method blan s, P , OP sam les for all matri ty es. anges ere determined at 2 standard deviations from the mean. ecause of the lo recoveries for these E S, the calculated lo er limits ere negative values. Therefore, the lo er limits have been set to 0 for these analytes.

Data for this table are derived from the single-laboratory validation study, and are only provided as examples for this draft method. The data will be updated to reflect the interlaboratory study results in a subsequent revision. Therefore, these criteria will change after interlaboratory validation. Several sections of this method state that Table 5 criteria are required, this is standard language that will be applicable when the method is finalized.

Table 6. Pooled MDL$_s$ and ML values from the Single-laboratory Validation Study, by Matrix[1]

	Aqueous (ng/L)		Solid (ng/g)		Tissue (ng/g)	
Compound	MDL$_s$	ML	MDL$_s$	ML	MDL$_s$	ML
P A	0.330	6.4	0.401	0.8	0. 3	2.0
P PeA	0.1 6	3.2	0.021	0.4	0.083	1.0
P A	0.318	1.6	0.020	0.2	0.0 6	0.
P A	0.221	1.6	0.02	0.2	0.088	0.
P OA	0.302	1.6	0.03	0.2	0.086	0.
P NA	0.221	1.6	0.086	0.2	0.160	0.
P DA	0.333	1.6	0.031	0.2	0.124	0.
P UnA	0.264	1.6	0.033	0.2	0.1 2	0.
P DoA	0.3	1.6	0.0	0.2	0.130	0.
P TrDA	0.238	1.6	0.038	0.2	0.086	0.
P TeDA	0.264	1.6	0.032	0.2	0.18	0.
P S	0.24	1.6	0.014	0.2	0.0 0	0.
P PeS	0.204	1.6	0.01	0.2	0.032	0.
P S[1]	0.21	1.6	0.018	0.2	0.083	0.
P S	0.13	1.6	0.0	0.2	0.043	0.
P OS[1]	0.32	1.6	0.06	0.2	0.2 4	0.
P NS	0.303	1.6	0.046	0.2	0.114	0.
P DS	0.334	1.6	0.040	0.2	0.101	0.
P DoS	0.1	1.6	0.038	0.2	0.1	0.
4 2 TS	2.281	6.4	0.282	0.8	0. 40	2.0
6 2 TS	3. 3	6.4	0.116	0.8	1.14	2.0
8 2 TS	1. 66	6.4	0.22	0.8	0.3 3	2.0
P OSA	0.22	1.6	0.068	0.2	0.0 4	0.
NMe OSA	0.1 6	1.6	0.04	0.2	0.161	0.
NEt OSA	0. 8	1.6	0.038	0.2	0.16	0.
NMe OSAA[1]	0. 86	1.6	0.030	0.2	0.0 3	0.
NEt OSAA[1]	0.324	1.6	0.044	0.2	0.138	0.
NMe OSE	1.1 1	16	0.203	2.0	. 8	.0
NEt OSE	1.022	16	0.24	2.0	1. 01	.0
PO-DA	0.406	6.4	0.136	0.8	0.161	2.0
ADONA	0.	6.4	0.0	0.8	0.082	2.0
P EESA	0.13	3.2	0.018	0.4	0.04	1.0
P MPA	0.1	3.2	0.033	0.4	0.0 0	1.0
P M A	0.11	3.2	0.02	0.4	0.06	1.0
N D A	1.384	3.2	0.084	0.4	0.2 4	1.0
C -P 3ONS	0.8 1	6.4	0.038	0.8	0.1 2	2.0
11C -P 3OUDS	0.81	6.4	0.0 1	0.8	0.312	2.0
3 3 TCA	0. 21	8.0	0.060	1.0	0.24	2.
3 TCA	.066	40	0.363	.0	1. 3	12.
3 TCA	. 42	40	0.308	.0	0.84	12.

[1] A standard containing a mi ture of branched and linear isomer of suitable uality to be used for uantitation is currently available and re uired to be used for all calibration, calibration verifications, and C sam les. f more become commercially available for other target analytes, they must be utili ed in the same manner.

Data for this table are derived from the single-laboratory validation study, and are only provided as examples for this draft method. The data will be updated with the pooled MDLs from the interlaboratory study results in a subsequent revision.

Table 7. Summary of Quality Control

Method Reference	Requirement	Specification and Frequency
Section 10.1	Mass Calibration	Annually and on as-needed basis
Section 10.1.	Mass Calibration erification	After mass calibration
Section 10.3	nitial Calibration (CA)	Minimum 6 calibration standards for linear model and calibration standards for non-linear models.
Sections 10.2.2, 14.4	etention Time (T) indo	After CA and at the beginning of analytical se uence
Sections .3.1, .4	E tracted nternal Standard (E S) Analytes	All CA standards, batch C and field sam les
Sections .3.2	Non-e tracted nternal Standards (N S)	All CA standards, batch C and field sam les
Sections .3.4, 10.3.1, 13.3	nstrument Sensitivity Chec (SC)	Daily, rior to analysis
Section 14.2	Calibration erification (C)	At the beginning and every 10 sam les
Section 14.6	nstrument lan	Daily rior to analysis and after high standards
Sections .1.3, . , 14.	Method lan (M)	One er re aration batch
Section 14.	Ongoing Precision ecovery (OP)	One er re aration batch
Section 11.0	imit of uantitation erification (OP)	Prior to analy ing sam les
Section 11.0	Matri S i e (MS MSD)	One er re aration batch (if re uired)

Table 8. Cross-reference of Abbreviations, Analyte Names, CAS Numbers for the Acid and Anion Forms of the Perfluoroalkyl carboxylates and Perfluoroalkyl sulfonates

Perfluoroalkyl carboxylic acids/anions				
Abbreviation	**Acid Name**	**CASRN**	**Anion Name**	**CASRN**
P A	Perfluorobutanoic acid	3 -22-4	Perfluorobutanoate	4 048-62-2
P PeA	Perfluoro entanoic acid	2 06- 0-3	Perfluoro entanoate	4 16 -4 -3
P A	Perfluorohe anoic acid	30 -24-4	Perfluorohe anoate	2612- 2-
P A	Perfluorohe tanoic acid	3 -8 -	Perflluorohe tanoate	12088 -2 -2
P OA	Perfluorooctanoic acid	33 -6 -1	Pefluorooctanoate	4 28 - 1-6
P NA	Perfluorononanoic acid	3 - -1	Perfluorononanoate	200 -68-2
P DA	Perfluorodecanoic acid	33 - 6-2	Perfluorodecanoate	382 -36-4
P UnA	Perfluoroundecanoic acid	20 8- 4-8	Perfluoroundecanoate	1 68 - 4-8
P DoA	Perfluorododecanoic acid	30 - -1	Perfluorododecanoate	1 1 8- -3
P TrDA	Perfluorotridecanoic acid	262 - 4-8	Perfluorotridecanoate	8623 4-8 -6
P TeDA	Perfluorotetradecanoic acid	3 6-06-	Perfluorotetradecanoate	36 1-8 -
Perfluoroalkyl sulfonic acids/anions				
P S	Perfluorobutanesulfonic acid	3 - 3-	Perfluorobutane sulfonate	4 18 -1 -3
P PeS	Perfluoro entansulfonic acid	2 06- 1-4	Perfluoro entane sulfonate	1 0 -36-
P S	Perfluorohe anesulfonic acid	3 -46-4	Perfluorohe ane sulfonate	10842 - 3-8
P S	Perfluorohe tanesulfonic acid	3 - 2-8	Perfluorohe tane sulfonate	14668 -46-
P OS	Perfluorooctanesulfonic acid	1 63-23-1	Perfluorooctane sulfonate	4 2 8- 0-6
P NS	Perfluorononanesulfonic acid	682 -12-1	Perfluorononane sulfonate	4 4 11-0 -4
P DS	Perfluorodecanesulfonic acid	33 - -3	Perfluorodecane sulfonate	12610 -34-8
P DoS	Perfluorododecanesulfonic acid	80-3 -	Perfluorododecane sulfonate	34362 -43-6

Table 9. Range of Recoveries for Extracted Internal Standards (EIS) in the Single-laboratory Validation Study, by Matrix

	Aqueous			Solid			Tissue		
	% Recovery		RSD	% Recovery		RSD	% Recovery		RSD
EIS Compounds	Min	Max	(%)	Min	Max	(%)	Min	Max	(%)
$^{13}C_4$-P A			1 .	3	113	3 .4	84		8.0
^{13}C -P PeA	3	103	13.3	28	112	1 .2	86	10	11.1
^{13}C -P A	3		2.		110	.	2		1.6
$^{13}C_4$-P A			2.4	3	111	6.0	80	3	8.2
$^{13}C_8$-P OA	8		0.8	86	11	4.4	0		2.8
^{13}C -P NA	82		1.6	8	110	4.2	0	8	4.3
$^{13}C_6$-P DA	1	3	3.3	8	112	4.	83		.
^{13}C -P UnA	6	4	6.	66	124	11.6	1	1	12.
$^{13}C_2$-P DoA	34	8	13.	26	10	24.3	4	6	2 .2
$^{13}C_2$-P TeDA	1	1 3	26.2	18	110	30.1	31	102	6 .8
$^{13}C_3$-P S	2	100	4.	8	120	.4	8	8	.1
$^{13}C_3$-P S			1.6	8	110	4.4	8		0.1
$^{13}C_8$-P OS	6	6	3.6		113	.	2	103	6.0
$^{13}C_2$-4 2 TS	81	1	14.8		248	1 .0	1 2	21	6.2
$^{13}C_2$-6 2 TS	64	183	16.4	6	12	.4	14	230	2 .2
$^{13}C_2$-8 2 TS	6	13	8.4	86	1 3	1 .2	136	220	24.6
$^{13}C_8$-P OSA	2	3	1 .4	61	123	10.0	8	6	4.
D_3-NMe OSA	14	4	16.4	28	86	22.	8	38	61.
D -NEt OSA	12	0	16.	21	0	2 .	8	30	.8
D_3-NMe OSAA	21	113	.3	2	142	14.8	106	13	13.1
D -NEt OSAA	12	106	8.2	68	1 1	16.		1 1	31.8
D -NMe OSE	11		18.6	13	10	2 .		30	81.1
D -NEt OSE	8	3	1 .6	16		30.4	0	2	103.1
$^{13}C_3$- PO-DA	2	113	2.0	0	11	10.4	3	102	.1

Data for this table are derived from the single-laboratory validation study, and are only provided as examples for this draft method. The data will be updated with the interlaboratory study results in a subsequent revision.

Table 10. Range of Recoveries for Non-Extracted Internal Standards in the Single-laboratory Validation Study, by Matrix

	Aqueous			Solid			Tissue		
	% Recovery		RSD	% Recovery		RSD	% Recovery		RSD
NIS Compounds	Min	Max	(%)	Min	Max	(%)	Min	Max	(%)
$^{13}C_3$-P A	60	1	10.3	4	8	6.4	1	82	.0
$^{13}C_2$-P A	43	4	18.6	2	0	.4	41	80	1 .3
$^{13}C_4$-P OA		8	.	4	8	6.4	1	82	.
^{13}C -P NA	64	8	.		4	.1	2	88	11.2
$^{13}C_2$-P DA		86	10.0		1	8.6	4	8	1 .4
$^{18}O_2$-P S		8	.6	3	8	.1	1	80	8.1
$^{13}C_4$-P OS	60	82	.	8	86	.0	2	8	10.3

Data for this table are derived from the single-laboratory validation study, and are only provided as examples for this draft method. The data will be updated with the interlaboratory study results in a subsequent revision.

21.0 Glossary

These definitions and purposes are specific to this method, but have been conformed to common usage to the extent possible.

21.1 Units of weight and measure and their abbreviations

21.1.1 Symbols

ºC	degrees Celsius
Da	Dalton (equivalent to "amu" below)
µg	microgram
µL	microliter
µm	micrometer
<	less than
≤	less than or equal
>	greater than
≥	greater than or equal
%	percent
±	plus or minus

21.1.2 Alphabetical abbreviations

amu	atomic mass unit (equivalent to Dalton)
cm	centimeter
g	gram
h	hour
L	liter
M	molar
mg	milligram
min	minute
mL	milliliter
mm	millimeter
cm	centimeter
m/z	mass-to-charge ratio
ng	nanogram
Q1	quantitation ion
Q2	confirmation ion
rpm	revolutions per minute
v/v	percent volume per volume

21.2 Definitions and acronyms (in alphabetical order)

Analyte – A PFAS compound included in this method. The analytes are listed in Table 1.

Calibration standard (CS) – A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the LC-MS/MS instrument.

Calibration verification standard (CV) – The mid-point calibration standard (CS-4) that is used to verify calibration. See Table 4.

CFR – Code of Federal Regulations

Compound - One of many variants or configurations of a common chemical structure. ndividual com ounds are identified by the number of carbon atoms and functional grou attached at the end of the chain.

Class A glassware olumetric glass are that rovides the highest accuracy. Class A volumetric glass are com lies ith the Class A tolerances defined in ASTM E6 4, must be ermanently labeled as Class A, and is su lied ith a seriali ed certificate of recision.

CWA Clean Water Act

Extracted internal standard (EIS) quantification The res onse of the target com ound is com ared to the res onse of the labeled analog of another com ound in the same OC.

LC i uid chromatogra h or li uid chromatogra hy

Internal standard A labeled com ound used as a reference for uantitation of other labeled com ounds and for uantitation of native P AS com ounds other than the com ound of hich it is a labeled analog. See nternal standard uantitation.

Instrument sensitivity check solution used to chec the sensitivity of the instrument. The solution contains the native com ounds at the concentration of the O .

Internal standard quantitation A means of determining the concentration of (1) a naturally occurring (native) com ound by reference to a com ound other than its labeled analog and (2) a labeled com ound by reference to another labeled com ound

IPR nitial recision and recovery four ali uots of a reference matri s i ed ith the analytes of interest and labeled com ounds and analy ed to establish the ability of the laboratory to generate acce table recision and recovery. An P is erformed rior to the first time this method is used and any time the method or instrumentation is modified.

Isotope dilution (ID) quantitation A means of determining a naturally occurring (native) com ound by reference to the same com ound in hich one or more atoms has been isoto ically enriched. The labeled P AS are s i ed into each sam le and allo identification and correction of the concentration of the native com ounds in the analytical rocess.

Isotopically labeled compound An analog of a target analyte in the method hich has been synthesi ed ith one or more atoms in the structure re laced by a stable (non-radioactive) isoto e of that atom. Common stable isoto es used are ^{13}C (Carbon-13) or Deuterium (D or ^{2}). These labeled com ounds do not occur in nature, so they can be used for isoto e dilution uantitation or other method-s ecific ur oses.

Limit of Quantitation (LOQ) The smallest concentration that roduces a uantitative result ith no n and recorded recision and bias. The O shall be set at or above the concentration of the lo est initial calibration standard (the lo est calibration standard must fall ithin the linear range).

Method blank An ali uot of reagent ater that is treated e actly as a sam le including e osure to all glass are, e ui ment, solvents, reagents, internal standards, and labeled com ounds that are used ith sam les. The method blan is used to determine if analytes or interferences are resent in the laboratory environment, the reagents, or the a aratus.

Method Detection Limit (MDL) The minimum measured concentration of a substance that can be re orted ith confidence that the measured analyte concentration is distinguishable from method blan results (40 C 136, A endi).

MESA Mining Enforcement and Safety Administration

Minimum level of quantitation (ML) The lo est level at hich the entire analytical system must give a recogni able signal and acce table calibration oint for the analyte. The M re resents the lo est concentration at hich an analyte can be measured ith a no n level of confidence. t may be e uivalent to the concentration of the lo est calibration standard, assuming that all method-s ecified sam le eights, volumes, and cleanu rocedures have been em loyed. Alternatively, the M may be established by multi lying the MD (ooled or un ooled, as a ro riate) by 3.18 and rounding the result to the number nearest to 1, 2, or 10^n, here n is ero or an integer (see 68 11 0).

MS Mass s ectrometer or mass s ectrometry

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Ali uots of field sam les that have been fortified ith a no n concentration of target com ounds, rior to sam le re aration and e traction, and analy ed to measure the effect of matri interferences. The use of MS MSD sam les is generally not re uired in isoto e dilution methods because the labeled com ounds added to every sam le rovide more erformance data than s i ing a single sam le in each re aration batch.

Multiple reaction monitoring (MRM) Also no n as selected reaction monitoring (S M). A ty e of mass s ectrometry here a arent mass of the com ound is fragmented through MS MS and then s ecifically monitored for a single fragment ion.

Must This action, activity, or rocedural ste is re uired.

NIOSH – The National nstitute of Occu ational Safety and ealth

Non-extracted internal standard (NIS) abeled P AS com ounds s i ed into the concentrated e tract immediately rior to injection of an ali uot of the e tract into the C-MS MS.

OPR Ongoing recision and recovery standard (OP) a method blan s i ed ith no n uantities of analytes. The OP is analy ed e actly li e a sam le. ts ur ose is to assure that the results roduced by the laboratory remain ithin the limits s ecified in this method for recision and recovery.

Precursor Ion or the ur ose of this method, the recursor ion is the de rotonated molecule (M- -) of the method analyte. n MS MS, the recursor ion is mass selected and fragmented by collisionally activated dissociation to roduce distinctive roduct ions of smaller *m/z*.

PFAS Per- and Polyfluoroal yl substances A grou of man-made fluorinated com ounds that are hydro hobic and li o hobic, manufactured and used in a variety of industries globally. These com ounds are ersistent in the environment as ell as in the human body. This method analy es for the P AS listed in Table 1.

Reagent water Water demonstrated to be free from the analytes of interest and otentially interfering substances at the method detection limit for the analyte.

Relative standard deviation (RSD) The standard deviation multi lied by 100 and divided by the mean. Also termed coefficient of variation.

Relative Standard Error (RSE) The standard error of the mean divided by the mean and multi lied by 100.

RF es onse factor. See Section 10.3.3.2.

RR elative res onse. See Section 10.3.3.2.

RT etention time**;** the time it ta es for an analyte or labeled com ound to elute off the P C UP C column

Should This action, activity, or rocedural ste is suggested but not re uired.

Signal-to-noise ratio (S/N) The height of the signal as measured from the mean (average) of the noise to the ea ma imum divided by the idth of the noise.

SPE Solid- hase e traction a techni ue in hich an analyte is e tracted from an a ueous solution or a solid tissue e tract by assage over or through a material ca able of reversibly adsorbing the analyte. Also termed li uid-solid e traction.

Stock solution A solution containing an analyte that is re ared using a reference material traceable to EPA, N ST, or a source that ill attest to the urity and authenticity of the reference material.

Appendix A - Sample Pre-screening Instructions

Sam les that are no n or sus ected to contain high levels of analytes may be re-screened using the follo ing rocedure. These are e am le rocedures using smaller sam le ali uots s i ed ith E S and N S and no clean u rocedures. Other re-screening rocedures may be used.

A ueous Sam les

1. Weight out 10 (0.1) g of sam le into a 0-m centrifuge tube.
2. Add 0 of E S and N S to the sam le and vorte to mi .
3. ilter 1 m of the sam le through 0.2- m membrane filter into a microvial. Sam le is ready for instrumental analysis.

Solid and Tissue Sam les

1. Weigh 1.0 (0.1) g sam le into 0-m oly ro ylene centrifuge tubes.
2. Add 20 m of 0.3 methanolic ammonium hydro ide (Section .1. .1). orte and mi on a sha er table (or e uivalent) for 10 min. Allo to settle and or centrifuge to roduce a clear e tract.
3. ilter using a Single Ste filter vial
   a. Add 20 of E S to a clean Single Ste filter vial (chamber).
   b. Add 400 of clear e tract from ste 2 (e.g., by adding e tract until it reaches the fill line), carefully vorte to mi .
   c. Use filter lunger art and filter.
4. Transfer 30 of filtrate to a 300- oly ro ylene micro-vial and dilute to 300 ith 0.3 methanolic ammonium hydro ide (Section .1. .1). Add N S to the filtrate.
. The e tract is no a 10 dilution.
6. Sam le is ready for instrumental analysis.

Calculate results using the e uivalent sam le eight com uted as follo s

$$Equivalent\ Weight = Sample\ weight\ (g) \times \frac{0.4\ mL}{20\ mL}$$

Note that the E S concentration in the diluted ortion is 0. the level in the regular analysis of solid sam les.

Appendix B - Aqueous Sample Subsampling Instructions

Warning: Because some target analytes may be stratified within the sample (e.g., AFFF-contaminated media, surfactants), or adhere to the walls of the sample container, subsampling may only be done on a project-specific basis. Subsampling has been shown to increase uncertainty in PFAS analysis, especially on foaming samples.

f a reduced sam le si e is re uired, transfer a eighed subsam le using the follo ing subsam ling rocedure to a 60-m DPE bottle and dilute to a ro imately 60 m using reagent ater. This container is no considered the sam le bottle.

1. ently invert sam le 3-4 times being careful to avoid foam formation and subsam le immediately (do not let stand).

2. f foam forms and more than m is re uired our sam le, avoiding any foam.

3. f foaming forms and a volume less than m is re uired i ette from cm belo the foam.

4. f no foam forms our or i ette based on volume re uired.