Other Test Method 45 (OTM-45) Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources

Background on OTM-45

The posting of a test method on the Other Test Methods portion of the Emission Measurement Center (EMC) website is neither an endorsement by EPA regarding the validity of the test method nor a regulatory approval of the test method. The purpose of the Other Test Methods portion of the EMC website is to promote discussion of developing emission measurement methodologies and to provide regulatory agencies, the regulated community, and the public at large with potentially helpful tools. Other Test Methods are test methods which have not yet been subject to the Federal rulemaking process. Each of these methods, as well as the available technical documentation supporting them, have been reviewed by the EMC staff and have been found to be potentially useful to the emission measurement community. The types of technical information reviewed include field and laboratory validation studies; results of collaborative testing; articles from peer-reviewed journals; peer review comments; and quality assurance (QA) and quality control (QC) procedures in the method itself. The EPA strongly encourages the submission of additional supporting field and laboratory data as well as comments regarding these methods.

These methods may be considered for use in federally enforceable State and local programs [e.g., Title V permits, State Implementation Plans (SIP)] provided they are subject to an EPA Regional SIP approval process or permit veto opportunity and public notice with the opportunity for comment. The methods may also be candidates to be alternative test methods to meet Federal requirements under 40 CFR Parts 60, 61, and 63. However, they must be approved as alternatives under Parts 60.8, 61.13, or 63.7(f) before a source may use them for this purpose. Consideration of a method's applicability for a particular purpose should be based on the stated applicability as well as the supporting technical information. The methods are available for application without EPA oversight for other non-EPA program uses including state permitting programs and scientific and engineering applications. As many of these methods are submitted by parties outside the Agency, the EPA staff may not necessarily be the technical experts on these methods. Therefore, technical support from EPA for these methods is limited, but the table at the end of this introduction contains contact information for the authors and developers so that you may contact them directly. Also, be aware that these methods are subject to change based on the review of additional validation studies or on public comment as a part of adoption as a federal test method, the Title V permitting process, or inclusion in a SIP.

Validated measurement methods are limited and under development for reliably identifying and quantifying if per- and polyfluoroalkyl substances (PFAS) are released into the air from stationary sources. The current lack of standardized methods to measure PFAS emissions and the limited availability of data on the performance of methods to measure PFAS introduce uncertainty in the understanding of the release of PFAS into the air from these sources. The lack of validated stationary source measurement methods for PFAS also leads to inconsistent findings, incomparable measurements, and lack of coordination between policy makers, facilities, and control technology development. This OTM provides a consistent method for use by the facilities, stationary source test teams, research laboratories, and other stakeholders to measure a common list of PFAS compounds released from vents and stacks. This OTM includes

performance based PFAS measurement tools and performance criteria developed through field application of this method.

The analytical method imbedded in OTM-45 may support a variety of measurement applications. The target compounds for this method are known PFAS compounds of concern which may be the focus of treatment or control as well as emerging industrial PFAS compounds of interest. This posting meets an agency commitment identified within the 2020 National Defense Authorization Act guidance for PFAS disposal and destruction. Posting this method, in and of itself, does not establish a requirement, although the use of this method may be specified by the EPA, state, or local authorities through independent actions. Terms such as "must" or "required," as used in this document, refer to procedures that are to be followed to conform with the method. References to specific brands and catalog numbers are included only as examples and do not imply endorsement of the products. Such reference does not preclude the use of equivalent products from other vendors or suppliers.

OTM-45 is a draft method under evaluation that will be updated as necessary when more data from stakeholders becomes available. Due to the need for consistency, this method is being released as an "Other Test Method (OTM)" by EPA's Emission Measurements Center to promote consistency with what we believe is the current best practices to sample and analyze the PFAS targets from stationary sources. We solicit feedback, comments, and additional data coming from the application of this method as we work to adjust this method in anticipation of potentially developing a reference method for PFAS from air emission sources. PFAS encompass a wide variety of compounds that can lead to different physical and chemical properties. As such, this method is not suitable for PFAS compounds that are not recoverable with the solvents used in this method. Addition of target compounds to this list require an evaluation of their performance in this method.

Note: Please submit a copy, either electronic or paper, of any test report from application of this OTM to EPA's Measurement Technology Group.

- **Electronic copies should be submitted via email with the subject line "OTM-045" to: EMC@epa.gov**
- **Paper copies should be mailed to:**
  Measurement Technology Group
  Office of Air Quality Planning and Standards
  U.S. Environmental Protection Agency (P.O. Box 12055, Mail Code E143-02)
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Summary of Major Changes included in Other Test Method 45 - (OTM-45) Revision 1 Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources

1. Addressed the appropriate use of PTFE and allowances for where it is reasonable and necessary and can be demonstrated non-interfering.

2. The number of pre-sampling standards has been expanded to five isotopically labeled compounds to better assess and indicate overall measurement performance.

3. The OTM-45 target analytes and respective pre-extraction isotopic labeled compounds used have been revised to be inclusive and consistent with EPA Office of Water (OW) Method 1633.

4. The OTM-45 extraction and cleanup reagents have been renamed "methanolic ammonium hydroxide" with the actual concentration of ammonium hydroxide in solution as opposed to the percentage of concentrated ammonium hydroxide in solution. This revision is also consistent with the nomenclature used in the EPA OW Method 1633.

5. A requirement and procedural clarification has been made to ensure that XAD-2 fraction concentration and preparation steps prior to analysis result in a solvent matrix containing at least 80% alkaline methanol. This revision includes an SPE recovery and concentration step which is a significant revision from the original OTM-45 procedure for processing fraction 2 and fraction 4.

6. Solid Phase Extraction, a streamlined approach known to successfully meet OTM-45 performance criteria, replaces evaporation concentration for XAD-2 sample recovery making the procedure a parallel to the impinger fraction recovery and concentration. SPE recommendations now include the use of WAX/GCB, 500mg/50mg/6cc SPE cartridges or equivalent. This SPE approach is presented to provide a detailed methodology that is known to be successful in meeting OTM-45 performance criteria. OTM-45 is a performance-based method. As a result, other approaches may be utilized provided they meet OTM-45 performance criteria. Section 9 of this method presents requirements for method performance.

7. Guidance on reporting fractions that are below method detection limits.

8. Eliminated the redundancy between Laboratory Sample Media Blank and Batch Blank Sample.

9. Other minor definition additions and editorial changes.

10. The requirement to perform a field train blank is now optional.

Other Test Method 45 - (OTM-45) Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources

1.0 Scope and Application

1.1 Applicability. OTM-45 is a performance-based method applicable to the collection and quantitative analysis of specific semivolatile and condensable per- and polyfluorinated alkyl substances (PFAS) in air emissions from stationary sources. This method can also be used for the collection and recovery of ionic and covalent PFAS for non-targeted analysis (NTA) of PFAS compounds. Table 45-1 of this method lists the individual target analytes that have been evaluated for measurement by OTM-45.

1.2 Scope. This method describes the sampling and sample recovery procedures used to measure individual semivolatile and particulate bound PFAS from stationary source air emissions. OTM-45 incorporates by reference some of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and sample preparation) from other methods that are essential to conducting OTM-45. To obtain reliable samples, source sampling teams must be trained and experienced with the following additional EPA test methods: Method 1; Method 2; Method 3; Method 4; and Method 5 of Appendices A-1, A-2, and A-3 to 40 Code of Federal Regulations (CFR) Part 60. Laboratory analysis teams must be trained and experienced in the use of liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) multiple reaction monitoring (MRM) as described in EPA Method 533 and Method 537.1

1.3 Branched and Linear PFAS Isomers

Both branched and linear PFAS isomers may be found in the environment. This method includes procedures for summing the contribution of multiple isomers to the final reported concentration. In those cases where standard materials containing multiple isomers are commercially available, laboratories should obtain such standards for the method analytes.

1.4 Performance Based. This method provides some flexibility for analysis of PFAS by including the addition of isotopically labeled standards in various parts of the sampling system to assess and evaluate method performance against criteria for successful sampling and analysis procedures. The laboratory may select LC columns, LC conditions, and MS conditions different from those used to develop the method. At a minimum, the pre-sampling standards, pre-extraction and the pre-analysis standards specified in the method must be used. Although OTM-45 provides specific procedures based on known and acceptable performance, users may modify the method to improve method performance, overcome interferences or to substitute superior materials and equipment, provided they use LC-MS/MS as the basis for separation and quantitation of method target compounds and meet all performance criteria in this method. Section 9 of this method presents requirements for method performance.

2.0 Summary of Method

This method identifies and determines the concentration in mass per unit gas volume sampled of specific PFAS in source emissions. Semivolatile and particulate bound target pollutants are withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber or quartz filter, on a packed column of adsorbent material and in a series of impingers. The target compounds are extracted from the individual sample collection media. The OTM-45 train results in four (4) discrete sample fractions, described in section 11.1 through 11.4, for analysis. The

extracts are analyzed by LC-MS/MS in the MRM detection mode. Quantification of each analyte is calculated using the isotope dilution technique. For QC purposes, the percent recoveries of the **pre-extraction standards** are calculated using the integrated peak areas of **pre-analysis standard(s)**, which are added to the final extract and function as traditional internal standards. The use of **pre-sampling standards** added to XAD-2 collection media prior to sampling and analyzed in the same manner as targeted PFAS compounds serves as an indication of the method's quantitative capture efficiency. This method is not intended to differentiate between target compounds in particulate-bound or gaseous fractions. This method uses isotopically labeled standards to improve method accuracy and precision.

3.0 Definitions

3.1 Alternate Recovery Standards. A group of isotopically labeled compounds that are not otherwise designated in this method for quality control purposes. Alternative recovery standards may be used as an additional step to assess the recovery of a compound or procedure in this method that is not already assessed as a mandatory part of this method.

3.2 Alternative Test Methods. Methods used to meet requirements in 40 CFR Parts 60, 61, and 63 that have been approved as substitutes for test methods specified in subparts to these parts.

3.3 Analysis Batch. A set of samples that are analyzed on the same instrument during a 24-hour period that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) standards. Additional CCCs may be required depending on the length of the Analysis Batch and the number of field samples.

3.4 Branched and Linear Isomers. Individual compounds with a common molecular formula, differing by the position of carbon and fluorine atoms attached to the structure.

3.5 Calibration Standard. A solution of the method analytes, pre-sampling standards, pre-extraction standards, and pre-analysis standard(s). The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.6 Chemical Abstract Service Registry Number (CASRN). CASRN is a unique identification number assigned by the Chemical Abstracts Service in the US to chemical substances described in the open scientific literature.

3.7 Continuing Calibration Check Standard (CCC). A calibration standard that is analyzed periodically to verify the accuracy of the existing calibration. The mid-point calibration standard is typically used to verify calibration. See Section 7.4.11 for analyte calibration ranges.

3.8 Extraction Batch. A set of field samples (not including QC samples) extracted together using the same lot of extraction devices, solvents, and spiking solutions.

3.9 Field Sample Media Blank (FSMB). Also called the field trip blank. The FSMB includes and represents the sampling media (i.e., filter, XAD-2 adsorbent) and reagents (i.e., impinger water contents, methanolic ammonium hydroxide rinsing solvents) associated with the field sample collection and recovery. The FSMB is treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, and all analytical procedures.

3.10 Initial Calibration (ICAL). ICAL is a statistically based calibration to establish the relationship between the analyzer response and known target compound concentrations across a defined range of concentration.

3.11 Isotope Dilution Technique. An analytical technique for measuring analyte concentration using the ratio of the peak area of the native analyte to that of an isotopically labeled analogue, that has been added to the original sample in a known amount and carried through the entire analytical procedure.

3.12 Isotopologue. An individual compound with an identical chemical formula and structure, differing only in isotopic composition.

3.13 Laboratory Fortified Media Blanks (LFMB). Also commonly referred to as Laboratory Control Samples. The LFMB includes and represents all the sampling media (i.e., filter, XAD-2 adsorbent) and reagents (i.e., impinger contents, rinsing solvents) associated with the field sample collection and recovery. Add 10 mL of deionized water and known quantities of the method analytes and isotope dilution analogues to the LFMB. The results of the LFMB verify method performance in the absence of sample matrix.

3.14 Laboratory Sample Media Blank (LSMB). The LSMB is intended to include and represent the sampling media (i.e., filter, XAD-2 adsorbent) and reagents (i.e., impinger contents, rinsing solvents) associated with the field sample collection and recovery, but is not actually shipped to the field and remains in the laboratory. The results of the LSMB verify that the sampling media and reagents are not introducing target analyte or interfering species.

3.15 Laboratory Fortified Sample Matrix Spike (LFSM) and Matrix Spike Duplicate (LFSMD). The LFSM and LFMSD are samples fortified using analyte Primary Dilution Standard (PDS). They are intended to evaluate post-extraction samples for bias due to matrix effects.

3.16 Method Detection Limit (MDL). The minimum qualitatively recognizable signal in laboratory analyses above background for a target compound with 99 percent confidence. Procedures for determining MDL are provided in Section 9.2.1.3.

Note: MDL is typically determined following 40 CFR Part 136 appendix B and includes samples prepared from blank media, spiked within 5 times of the expected MDL and processed in a manner identical to field sample preparation.

3.17 Multiple Reaction Monitoring (MRM). A targeted mass spectrometry technique that selects a precursor ion for subsequent fragmentation to product ions that are used to confirm target identification and quantitate target compounds. This allows the detection and quantification of specific molecules in a complex mixture.

3.18 Perfluorinated Alkyl Substances. Aliphatic substances where all hydrogen (H) atoms attached to carbon atoms have been replaced by fluorine (F) atoms, except those H atoms whose substitution would modify the nature of any functional groups present.

3.19 PFOA means perfluorooctanoic acid.

3.20 PFOS means perfluorooctanesulfonic acid.

3.21 PFHxS means Perfluoro-1 -hexanesulfonic acid.

3.22 Polyfluorinated Alkyl Substances. Aliphatic substances where all hydrogen atoms attached to at least one (but not all) carbon atoms have been replaced by F atoms.

3.22 Pre-analysis Standard(s). Pre-analysis standard(s) are quality control compounds that are added to all standard solutions and to extracts immediately prior to analysis 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 pre-analysis standard(s) are isotopically labeled analogues as listed in Table OTM-45-3. The pre-analysis standard(s) are indicators of instrument performance and are used to calculate the recovery of the pre-extraction standards through the extraction procedure. In this method, the pre-analysis standard(s) are not used in the calculation of the recovery of the native analytes. Pre-analysis standard(s) are added to every sample (including blank, quality control sample, and calibration solutions) at a known amount.

Note: Pre-analysis standard(s) is identical to Isotope Performance Standards in Method 533.

3.23 Precursor Ion. The gas-phase species corresponding to the method analyte that is produced in the electrospray ionization interface of the LC-MS/MS. During tandem mass spectrometry, or MS/MS, the precursor ion is mass selected and fragmented by collision-activated dissociation to produce distinctive product ions of smaller mass to charge (m/z) ratio. For this method, the precursor ion is usually the deprotonated molecule of the method analyte, except for Hexafluoropropylene oxide-dimer acid (HFPO-DA). For this analyte, the precursor ion is formed by decarboxylation of HFPO-DA.

3.24 Pre-extraction Standard(s). A group of isotopically labeled analogues of the method analytes that are added in a known amount to all standard solutions, to each field sample and

field blank (i.e., the primary and secondary XAD-2 adsorbent traps, filter, and impinger samples), and to laboratory blanks immediately before extraction. The pre-extraction standards are also the quantification reference compounds used to quantify the native target compounds present in the sample and correct for biases associated with extraction, cleanup, and concentration recovery.

Note: Not all target method analytes currently have an isotopically labelled analogue. In these cases, an alternative isotopically labelled quantification reference compound analogue is recommended in Table 45-1 until such time as the isotopically labelled analogue is available.

3.25 Pre-sampling Standard(s). A group of isotopically labeled analogues of the method analytes added in a known amount to the XAD-2 adsorbent prior to sampling and are indicators of overall measurement performance.

3.26 Primary Dilution Standard (PDS). A solution that contains method analytes (or QC analytes) prepared from stock standards. PDS solutions are used to fortify QC samples and diluted to prepare calibration standards. NOTE: Multiple PDS solutions are used: see section 7 for descriptions of each.

3.27 Product Ions. One or more fragment ions that are produced in MS/MS by collision activated dissociation of the precursor ion.

3.28 Quality Control Standard (QCS). A standard containing method target compounds prepared independently from the calibration solutions. For this method, the QCS is a repeat of the entire dilution scheme starting with the same stock materials (neat compounds or purchased stock solutions) used to prepare the primary calibration solutions. Independent sources and separate

lots of the starting materials are not required, provided the laboratory has obtained the purest form of the starting materials commercially available. The purpose of the QCS, prepared at the middle concentration of the calibration range, is to verify the integrity of the calibration standards.

3.29 Quantitative Reporting Limit (QRL). The minimum quantitative level that can be reported. The QRL is based on the lowest concentration of target compound(s) used during calibration. Being sample specific, the QRL is affected by sample size, dilution, aliquots, etc.

3.30 Relative Response Factor (RRF). The response of the mass spectrometer to a known amount of an analyte relative to the response to a known amount of an isotopically labeled standard.

3.31 Sampling Train Field Blank (STFB). The complete field assembly and recovery of an OTM-45 sampling train after actual sampling and recovery including reassembling a sampling train after sample recovery, bringing the train to sampling location, heating and leak checks. The STFB is conducted using glassware that has been previously used for emissions sampling as part of the current field test. The purpose of the STFB is to determine if method analytes or other interferences are introduced into the sample from previous sample runs using previously sampled sample train glassware.

3.32 Sampling Train Proof Blank (STPB). The complete field assembly and recovery of a clean OTM-45 sampling train without actual sampling, including bringing the train to sampling location, heating, and leak checks. The STPB is conducted using clean glassware that has not been previously used for emissions sampling as part of the current field test. The purpose of the STPB is to determine if method analytes or other interferences are introduced into the sample

from the clean, unused sample train glassware, train assembly, preparation, and recovery, including the field environment.

3.33 Semivolatile and Condensable PFAS. Poly and perfluoro compounds with boiling points above 100°C.

3.34 Stack Detection Limit (SDL). The minimum qualitatively recognizable gaseous stack concentration above background for a target compound. The SDL is a mathematically derived from the MDL for each sample fraction, the total gaseous stack sample volume collected, and the sample preparation steps in this method. Each sample fraction in this method has a distinct MDL based on the sample preparation, concentration, and aliquot splitting performed during the sample analysis procedures. Being sample specific, the SDL is affected by stack sample volume, sample extract volume, sample concentration, sample splits, and dilution, etc. The SDL is based on the sum of sample fractions 1-3 MDLs and the run-specific gaseous sample volume. The SDL is calculated using the equation 45-15 in section 12.6.3.1 of this method.

4.0 Interferences

4.1 Organic Compounds. Very high amounts of other organic compounds in the matrix may interfere with the analysis. This method provides examples of extraction and cleanup procedures to reduce, but not necessarily eliminate, matrix effects due to high concentrations of organic compounds.

4.2 Target compound contaminants or related organics in solvents, reagents, glassware, isotopically labeled spiking standards, and other sample processing hardware are potential method interferences. Routinely evaluate all these materials to demonstrate that they are either

free from interferences under the conditions of the analysis, or that the interference does not compromise the quality of the analysis results. Evaluate chemical interference through the preparation and analysis of LSMBs. Use high purity reagents, solvents, and standards to minimize interference problems in sample analysis.

4.3 PTFE products, including PTFE cap liners, can be a source of PFAS contamination. The use of PTFE in this method must be avoided or PTFE products must be tested and shown to be contaminant free before use. Polypropylene (PP) or polyethylene (PE, HDPE) products may be used in place of PTFE products to minimize PFAS contamination.

4.4 Labeled standards may include trace quantities of native PFAS and should be screened or certified pure before use.

4.5 Following extraction, aqueous samples should not come into contact with any glass containers or pipettes as PFAS can potentially adsorb to glass surfaces. The eluate must be collected in a polypropylene tube prior to concentration to dryness. Concentration to dryness in glass tubes may cause poor recovery. Standards dissolved in organic solvent may be purchased in glass ampoules. These standards in organic solvent are acceptable and subsequent transfers may be performed using glass syringes and pipets.

4.6 Fluorotelomer Sulfonates. Three fluorotelomer sulfonates in the analyte list (4:2FTS, 6:2FTS, and 8:2FTS) are referenced to their $^{13}C_2$ isotope dilution analogue. The mass difference between the telomer sulfonates and the pre-extraction standards is 2 mass units. The single sulfur atom in each of the unlabeled molecules has a naturally occurring M+2 isotope (^{34}S) at 4.25%. Thus, the precursor ions of the $^{13}C_2$ isotopically labeled analogues and the naturally occurring ^{34}S

analogues present in the native analytes have the same nominal masses. The product ions of the telomer sulfonate pre-extraction standards listed in Table 45-2 would contain a small contribution from the ^{34}S analogue of the native telomer sulfonates. At the concentrations specified in this method, the contribution of the ^{34}S analogue to the isotope dilution analogue was not greater than 2.7%. Alternate product ions may be used if there is sufficient abundance.

5.0 Safety

Note: Develop a safety program for the handling of PFAS to avoid contact with sampling media and sample recovery solutions.

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all safety issues associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this method.

5.2 Commercial Standards. This method recommends that the laboratory purchase dilute standard solutions of the analytes required for this method. However, if preparing primary solutions, use a hood or glove box. Personnel handling primary solutions should wear personal protective equipment including nitrile gloves.

5.3 Toxicity. The toxicity or carcinogenicity of other reagents or chemicals used in this method is not precisely defined. However, treat each chemical as a potential health hazard and minimize exposure to these chemicals. The field and laboratory staff are responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. Ensure that a reference file

or list of internet sites that contain safety data sheets (SDS) is available to all personnel involved in the sampling and chemical analysis of samples known or suspected to contain PFAS.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Apparatus and materials other than those specified in this method may achieve equivalent performance. Meeting the performance requirements of this method is the responsibility of the source testing team and laboratory team.

6.1 Sampling Train. Figure OTM-45-1 of this method shows a schematic of the OTM-45 sampling train. The OTM-45 sampling train is a modification of standard Method 5 from 40 CFR Part 60 Appendix A with adaptation from the SW-846 Method 0010 sampling train.

6.1.1 Nozzle. The nozzle must be made of quartz or borosilicate glass or titanium. Stainless steel nozzles may not be used.

6.1.2 Probe Liner. Use either borosilicate, or quartz glass probe liners with a heating system capable of maintaining a probe gas temperature of 120 ± 14 °C (248 ± 25 °F) during sampling. Use a graphite ferrule to achieve the seal at the nozzle end of the probe for stack temperatures up to about 300 °C (572 °F). Use a quartz glass liner and integrated quartz nozzle for stack temperatures between 300 and 1,200 °C (572 and 2,192 °F). Alternatives such as Hastelloy or Inconel for high temperature sources are an option.

Note: PTFE ferrule or single use PTFE coated O-ring may be used if demonstrated to meet the clean equipment requirement in Section 9.2.2.1.

6.1.3 Filter Holder and Support. Use a filter holder of borosilicate glass with a drilled and channeled (not fritted) filter support. The filter holder design must provide a positive seal against leakage from the outside or around the filter. The filter holder must be durable, easy to load, leak-free in normal applications, and positioned immediately following the probe and cyclone bypass (or cyclone, if used) with the active side of the filter perpendicular to the source of the flow. The filter support may be PTFE or titanium (preferred). Stainless-steel filter supports may not be used. If a PTFE filter support is used, it must be evaluated for PFAS contamination and meet the clean equipment requirement in Section 9.2.2.1.

6.1.4 Filter Heating System. Use any heating system capable of monitoring and maintaining the temperature around the filter to ensure that the sample gas temperature exiting the filter is above the dew point for water or default to 120 ± 14 °C (248 ± 25 °F) during sampling. Other temperatures (e.g., 10 °C above the stack temperature) may be used as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Sampling sources with entrained water droplets requires use of probe and filter temperatures to vaporize water to avoid damaging the filter.

6.1.5 Filter Temperature Sensor. Install a temperature sensor capable of measuring temperature to within ± 3 °C (5.4 °F). The sensing tip of the sensor may be encased in glass or metal and must protrude at least 1.3 centimeters (cm) (½ in.) into the sample gas exiting the filter.

6.1.6 Sample Transfer Line. The sample transfer line is used to transport gaseous emissions from the heated filter holder to the condenser when they cannot be directly connected. The sample transfer line must be capable of meeting the operational requirements in 8.1.5 for combustion and non-combustion sources.

6.1.6.1 The sample transfer line must be heat traced and be constructed of glass whenever possible with connecting fittings that form leak-free, vacuum-tight connections without using sealing greases or tapes.

6.1.6.2 When sample transfer lines are necessary and glass construction is not possible, HDPE or PFA sample transfer lines may be used. If an HDPE or PFA sample transfer is necessary, it must be cleaned (e.g., heated and purged with nitrogen for several hours prior to collecting the samples) and evaluated to meet requirements in Section 9.1.2 for PFAS contamination.

Note: Due to temperature compatibility, the HDPE sample transfer line is limited to non-combustion sources.

6.1.6.3 The heated sample line must be included in the sample train proof blank (STPB) train described in 9.1.3 and meet the STPB QA/QC criterion listed in Table 45-5.

Note: The use of a long sample transfer line should be avoided if possible. Orient the sample transfer lines with the downstream end lower than the upstream end so that any condensate will flow away from the filter and into the condenser.

6.1.7 Condenser. Glass, water-jacketed, coil-type with compatible fittings. Orient the condenser to cause moisture to flow down to the adsorbent module to facilitate condensate drainage. Figure OTM-45-2 of this method shows a schematic diagram of the condenser.

6.1.8 Water Circulating Bath. Use a bath pump circulating system capable of providing chilled water flow to the condenser and adsorbent module water jackets. A submersible pump is placed in the impinger ice water bath to circulate the ice water contained in the bath. Install a

temperature sensor capable of measuring temperature to within ± 3 °C (5.4 °F) so that the sensing tip protrudes at least 1.3 centimeters (cm) (1⁄2 in.) into the sample gas exiting the condenser. Encase the sensing tip of the sensor in glass or PTFE if needed. Verify the function of this system by measuring the gas temperature at the entrance to the adsorbent module. Maintain this temperature at < 20 °C (68 °F).

6.1.9 Primary and Secondary Adsorbent Module. Use a water-jacketed glass container to hold up to 40 grams (g) of the solid adsorbent. Figure OTM-45-2 of this method shows a schematic diagram of the adsorbent module. Other physical configurations of the adsorbent resin module/condenser assembly are acceptable if the configuration contains the requisite amount of solid adsorbent and maintains the minimum length-to-width adsorbent bed ratio of two-to-one. Orient the adsorbent module vertically to facilitate condensate drainage. The modules must include a temperature sensor described in Section 6.1.5 of this method. The connecting fittings must form leak-free, vacuum-tight seals. Include a coarse glass frit in the adsorbent module to retain the adsorbent.

6.1.10 Impingers. Use four or five impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger is a water knockout impinger and must be a short-stem (water-dropout) design or equivalent. The second, fourth, and fifth impingers must be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1⁄2 in.) inside diameter (ID) glass tube extending to approximately 1.3 cm (1⁄2 in.) from the bottom of the flask. The third impinger must be of the Greenburg-Smith design with the standard tip. The second, third, and fourth impingers must contain known quantities of water, the fifth impinger is used to contain a known weight of silica gel or equivalent desiccant.

6.2 Sample Recovery Equipment.

6.2.1 Fitting Caps. Use leak-free ground glass fittings or any similar leak-free non-contaminating fitting to cap the sections of the sampling train exposed to the sample gas.

6.2.2 Wash Bottles. Use high density polyethylene (HDPE) bottles.

6.2.3 Probe-Liner, Probe-Nozzle, and Filter-Holder Brushes. Use inert bristle brushes with precleaned stainless steel handles. Extensions of the probe brush must be made of stainless steel and be at least as long as the probe. Use brushes that are properly sized and shaped to remove accumulated material from the nozzle and probe liner if used.

6.2.4 Filter Storage Container. Use a sealed filter holder, wide-mouth amber glass jar with HDPE-lined cap, or glass petri dish sealed with HDPE tape or encased in a resealable polyethylene bag. Purchase precleaned amber glass jars and petri dishes or clean according to the glassware cleaning procedures listed in Section 8.1.1.1 of this method.

6.2.5 Field Balance. Use a weighing device capable of measurements to an accuracy of 0.5 g.

6.2.6 Aluminum Foil. Use heavy duty aluminum foil cleaned by rinsing three times with methanolic ammonium hydroxide (1.5% v/v) and stored in a pre-cleaned glass petri dish or glass jar. Do not use aluminum foil to wrap or contact filter samples due to the possibility of reaction between the sample and the aluminum.

6.2.7 Silica Gel Storage Containers. Use an air-tight container to store silica gel.

6.2.8 Sample Storage Containers. Recover samples in high density polyethylene (HDPE) bottles, 125, 250, 500- or 1000-milliliters (mL) with leak-free polyethylene-lined caps. Either purchase precleaned bottles or clean containers according to glassware cleaning procedures listed in Section 8.1.1.1 of this method.

6.3 Sample Extraction Equipment.

6.3.1 Sample Containers. Use 125- and 250-mL HDPE bottles with polypropylene or polyethylene-lined caps.

6.3.2 Test Tubes. Use polypropylene test tubes or small (e.g., 5 to 15 mL) polypropylene vials with polypropylene screw caps.

6.3.3 Nitrogen Evaporative Concentrator. Use a nitrogen evaporative concentrator equipped with a water bath with the temperature controlled in the range of 30 to 60 °C (86 to 140 °F) (N-Evap Organomation Associates, Inc., South Berlin, MA, or equivalent).

6.3.4 Shaker Table. Use a shaker table (Eberbach Shaker Model E6013, Eberbach Corporation, Belleville, MI, or equivalent) capable of holding samples securely and operating uninterrupted for at least 18 hours.

6.3.5 Filter Paper (0.45 µm pore size). Filter extract from “front half” probe filter before concentration step.

6.3.6 Digestion Block (“hot block”). Use a digestion block capable of reaching 55-60 °C and securely holding digestion vessels. Used for concentration of extracts.

6.3.7 Digestion Vessels. Use polypropylene digestion vessels capable of holding 70 mL.

6.3.8 Watch Glass. Use ribbed polypropylene watch glass capable of covering digestion vessels.

6.4.1 Pasteur Pipettes. Use disposable pipettes, or serological pipettes typically 150 mm long x 6 mm ID.

6.5 Solid Phase Extraction (SPE).

6.5.1 SPE Cartridge. (Phenomenex Strata PFAS WAX/GCB, 500mg/50mg/6cc) SPE cartridges containing weak anion exchange, mixed-mode polymeric sorbent (polymeric backbone and a diamino ligand), particle size approximately 85 μm. The SPE sorbent must have a pKa above 8 so that it remains positively charged during extraction. SPE cartridges contain 500 mg sorbent.

6.5.1.1 SPE Cartridge Interferences. Solid phase extraction cartridges may be a source of interferences. The analysis of LSMBs provides important information regarding the presence or absence of such interferences. Each brand and lot of SPE devices must be tested as part of the LSMB to ensure that contamination does not preclude analyte identification and quantitation. SPE cartridges must be sealed during storage to prevent ambient contamination of the SPE sorbent.

6.5.2 Vacuum Extraction Manifold. Equipped with flow and vacuum control [e.g., Supelco Cat. No. 57030-U, UCT Cat. No. VMF016GL (the latter requires UCT Cat. No. VMF02116 control valves), or equivalent systems]. Automated devices designed for use with SPE cartridges may be used; however, all extraction and elution steps must be the same as in the manual procedure. Care must be taken with automated SPE systems to ensure that Teflon tubing and other PTFE

components commonly used in these systems, do not contribute to unacceptable analyte concentrations in LSMBs.

6.5.3 Sample Delivery System. Use of large volume sampling lines, constructed with polyethylene tubing, are recommended, but not mandatory. Large volume sample transfer lines, constructed with PTFE tubing, are commercially available for standard extraction manifolds (e.g., Supelco Cat. No. 57275 or equivalent). The PTFE tubing can be replaced with 1/8" o.d. x 1/16" i.d. polyethylene tubing [Freelin-Wade (McMinnville, Oregon) LLDPE or equivalent] cut to an appropriate length. This prevents potential contamination from PTFE transfer lines. Other types of non-PTFE tubing may be used provided it meets the LSMB and LFMB QC requirements. PTFE tubing may be used, but an LSMB must be run on each individual transfer line and the QC requirements in Section 9.2.2.1 must be met. In the case of automated SPE, the removal of PTFE lines may not be feasible; therefore, acceptable performance for the LSMB must be met for each port during the Initial Demonstration of Capability (IDC) (Section 9.2.1). LSMBs must be rotated among the ports during routine analyses thereafter. Plastic reservoirs are difficult to rinse during elution and their use may lead to lower recovery.

6.6 LC-MS/MS System.

6.6.1 LC System. The LC system must provide consistent sample injection volumes and be capable of performing binary linear gradients at a constant flow rate.

Note: On some LC systems, PFAS may build up in PTFE transfer lines when the system is idle for more than one day. To prevent long delays in purging high levels of PFAS from the LC solvent lines, it may be useful to replace PTFE tubing with polyetheretherketone (PEEK) tubing

and the PTFE solvent frits with stainless steel frits. A delay column, HLB Direct Connect 2.1 x 30 mm (Waters 186005231), was placed in the mobile phase flow path immediately before the injection valve. This direct connect column may have reduced the co-elution of PFAS originating from sources prior to the sample loop from the PFAS injected in the sample. It may not be possible to remove all PFAS background contamination.

6.6.2 Chromatography Column. C18 liquid chromatography column (2 x 50 mm) packed with 3μm C18 solid phase particles (Phenomenex Part Number 00B-4439-B0 or equivalent).

6.6.3 Electrospray Ionization Tandem Mass Spectrometer (ESI-MS/MS). The mass spectrometer must be capable of electrospray ionization in the negative ion mode. The system must be capable of performing MS/MS to produce unique product ions for the method analytes within specified retention time segments. A minimum of 10 scans across the chromatographic peak is needed to ensure adequate precision. Some ESI-MS/MS instruments may not be suitable for PFAS analysis. For this method, the m/z 80 product ion must be used for PFOS and PFHxS to minimize this problem and promote comparability between laboratories. Some MS/MS instruments may not be able to scan a product ion with such a wide mass difference from the precursor ion. These instruments may not be used for this method if PFOS or PFHxS analysis is to be conducted.

6.6.4 MS/MS Data System. An interfaced data system is required to acquire, store, and output MS data. The computer software must have the capability of processing stored data by recognizing a chromatographic peak within a given retention time window. The software must allow integration of the abundance of any specific ion between specified time or scan number limits. The software must be able to reproducibly integrate analyte and internal standard ion

abundances to construct calibration curves and calculate analyte concentrations using the isotope dilution technique.

7.0 Reagents, Media, and Standards

Unless otherwise indicated, all reagents must conform to the *Specifications and Procedures for Reagents and Standard-Grade Reference Materials*. Reagent grade or better chemicals must be used. Unless otherwise indicated, all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used if the reagent is demonstrated to be free of analytes and interferences and all requirements in Section 13 are met when using these reagents media and standards.

7.1 Sampling Media.

7.1.1 Filter. Glass or Quartz fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron di-ethyl-hexyl-sebacate (DEHS) particles or equivalent. Guidance for high efficiency filter testing can be found in ISO 29463-1, ISO 29463-2, ISO 29463-3 and ISO 29463-4.

7.1.1.1 Filter Quality Control Check. Conduct a filter lot blank evaluation prior to the field test to demonstrate that filters are free from contamination or interference. Perform extraction and analysis using the same procedures used to process field samples as outlined in Section 11 of this method on a minimum of three filters from the lot. The blank filter check analysis must meet the performance requirements in Section 9.2.2.1 of this method.

7.1.2 Adsorbent Resin (Amberlite® XAD–2 Resin). All adsorbent resin must meet the cleanliness criteria in Section 9.2.2.1 of this method for all target compounds on the analysis list following the same extraction, concentration, cleanup, and analysis steps as field samples. This method recommends using the procedures provided in the Appendix to clean the resin before use, if needed. However, this method allows alternative cleanup procedures that use automated extraction equipment if the adsorbent meets the required performance criteria in Section 9.2.2.1 of this method.

7.1.3 Conduct a quality control check on each batch of cleaned adsorbent. Perform extraction and analysis using the same procedures used to process field samples as outlined in Section 11 of this method on a quantity of the sorbent representative of the amount typically packed into a sampling module. The cleaned adsorbent must meet the criteria in Section 9.2.2.1 of this method. A LSMB conducted on a filter and adsorbent lot combination used for a test can serve this purpose.

7.1.3.1 Storage. Store cleaned adsorbent in its original purchase container that has been cleaned according to the procedure in Section 8.1.1.1 of this method, a clean wide-mouth HDPE container with a polypropylene or polyethylene-lined cap, or in clean glass adsorbent modules tightly sealed with glass caps.

7.1.4 Glass Wool. Clean the glass wool to meet the specifications in Section 9.2.2.1 of this method. Using sequential immersion in three clean aliquots of methanolic ammonium hydroxide (1.5% v/v), drying in a 110 °C (230 °F) oven, and storing in a methanolic ammonium hydroxide (1.5% v/v) rinsed glass jar with a polypropylene or polyethylene-lined screw cap can meet these requirements.

7.1.5 Water. Use deionized or distilled PFAS free water meeting requirements in Section 9.2.2.1 of this method and store in its original container or in a methanolic ammonium hydroxide (1.5% v/v)-rinsed glass container with a polypropylene or polyethylene-lined screw cap.

7.1.6 Silica Gel. Indicating type, 6–16 mesh. If previously used, dry at 175 °C (347 °F) for two hours. Use new silica gel as received. Other types of desiccants may be used provided they perform as well or better.

7.2 Sample Recovery, Cleanup, and Extraction Reagents.

7.2.1 Methanol. CH_3OH, CASRN 67-56-1, LC grade (Fisher Scientific, Cat. No. A456 or equivalent). PFAS free meeting requirements in Section 9.2.2.1 of this method and store in its original container or in a methanolic ammonium hydroxide (1.5% v/v)-rinsed glass container with a polypropylene or polyethylene-lined screw cap.

7.2.2 Concentrated Ammonium Hydroxide Solution. NH_4OH, CASRN 1336-21-6, approximately 30% in water as ammonia, approximately 14.5 N (Fisher Scientific, Cat. No. A669, Certified ACS Plus grade, or equivalent).

7.2.3 Methanolic ammonium hydroxide (1.5% v/v). Prepared by diluting of 50 mL concentrated ammonium hydroxide solution (30%) into 1 L final volume in methanol.

7.2.4 Methanolic ammonium hydroxide (1% v/v). Prepared by diluting 33 mL of concentrated ammonium hydroxide solution (30%) into 1 L final volume in methanol.

7.2.5 Methylene Chloride. Reagent grade. Used to clean XAD-2 sorbent.

7.3 Standard Solutions.

7.3.1 Stability of Methanolic Solutions.

Fluorinated carboxylic acids will esterify in anhydrous acidic methanol. To prevent esterification, standards must be stored under basic conditions. If base is not already present, this may be accomplished by the addition of ammonium hydroxide (approximately 4 mole equivalents) when standards are diluted in methanol. When calculating molarity for solutions containing multiple PFAS, the molecular weight can be estimated as 250 atomic mass units. It is necessary to include ammonium hydroxide in solutions of both isotopically labeled and native analytes. The grams per liter of ammonium hydroxide needed may be calculated using the following equation:

$$\frac{Total\ PFAS\ mass(g) x\ 160\left(\frac{g}{mol}\right)}{250\left(\frac{g}{mol}\right)} = Mass\ of\ NH_4OH\ Required\ (g) \qquad \text{Eq. 45-1}$$

7.3.2 Preparation of Standards.

When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. PFAS analyte and isotopically labeled analogues commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be stored in polypropylene containers.

The PDS concentrations for the method are listed in the Table 45-3. Solution concentrations listed in this section are included as examples. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification should be prepared in the smallest volume that can be accurately measured

to minimize the addition of excess organic solvent to aqueous samples. The analyte supplier's guidelines are used to determine when standards need to be replaced.

7.3.3 Storage Temperatures for Standard Solutions. Store stock standards at less than 4 °C unless the vendor recommends otherwise. The PDS may be stored at any temperature, but cold storage is recommended to prevent solvent evaporation. PDS stored at –20 °C showed no change in analyte concentrations over a period of 6 months.

7.3.4 Pre-analysis Standard(s). Obtain the pre-analysis standard(s) as certified standard solutions, if available, or as the neat compounds. (Note: that CASRNs are not currently available for these compounds.) One or more of the pre-analysis standards listed in Table 45-3 must be used. The final sample extracts are fortified with the pre-analysis standard(s) to yield a recommended concentration of 10 ng/mL of each pre-analysis compound.

Note: Additional pre-analysis standard(s) may be used provided they are isotopically labeled analytes or labeled analytes with similar functional groups as the method analytes. Linear isomers are recommended to simplify peak integration. Method modification QC requirements must be met (Sect. 9.3) whenever additional pre-analysis standard(s) are used. The final sample extracts are fortified with 10 μL of the pre-analysis standard(s) to yield a concentration of 10 ng/mL for each pre-analysis standard.

7.3.5 Pre-analysis Primary Dilution Standard (Pre-analysis Standard(s)-PDS). Prepare the pre-analysis standard(s)-PDS in the methanolic ammonium hydroxide (1.5% v/v) extraction solution to prevent esterification.

7.3.6 Pre-extraction Standards. Obtain the isotopically labeled analogues listed in Table 45-1 as individual certified standard solutions or as certified standard mixes. The listed isotope dilution analogues are recommended and correspond to other methods that measure the same target compounds. Pre-extraction isotopically labeled compounds must be analogs of the target compound if available. Linear isomers are recommended to simplify peak integration.

Note: Chemical Abstracts Registry Numbers are not currently available for these isotopically labeled analogues.

7.3.6.1 Pre-extraction PDS. Prepare the pre-extraction standards in methanol from their standards and add ammonium hydroxide if not already present to prevent esterification as described in Section 7.3.1. Samples are fortified with the pre-extraction standards PDS to yield concentrations of 40 – 160 ng/sample fraction.

7.3.7 Pre-sampling PDS. Prepare the pre-extraction standards listed in Table 45-3 in methanolic ammonium hydroxide (1.5% v/v) to prevent esterification as described in Section 7.3.3.

7.3.8 Analyte Standard Materials. Analyte standards may be purchased as certified standard solutions or prepared from neat materials of assayed purity. If available, the method analytes should be purchased as technical grade to ensure that linear and branched isomers are represented. Standards or neat materials that contain only the linear isomer can be substituted if technical-grade analytes are not available as quantitative standards. Stock standards are made by dilution in methanolic ammonium hydroxide (1.5% v/v) solution (as described in Section 7.2.3). Technical grade, quantitative PFHxS and PFOS standards containing branched and linear isomers must be used when available.

7.3.9 Correction for Analytes Obtained in the Salt Form. This method measures all forms of the analytes as anions. The identity of the counterion in PDS used for calibration needs to be considered for results reported in mass per volume in emission calculations. Analytes may be commercially available as neat materials or as certified stock standards as their corresponding ammonium, sodium, or potassium salts. These salts are acceptable standards provided the measured mass, or concentration, is corrected for the salt content. The equation for this correction is provided below.

$$mass(acid\ form) = mass(salt\ form)x\ \frac{MW\ acid}{MW\ salt}$$ Eq. 45-2

7.3.10 Native Analyte PDS. The analyte PDS is used to prepare the calibration standards and to prepare the laboratory blanks (LFMBs) with the method analytes. Prepare the analyte PDS by combining and diluting the analyte stock standards in 100% methanol and add ammonium hydroxide if not already present to prevent esterification. Select nominal analyte concentrations for the PDS such that between 5 and 100 µL of the PDS is used to fortify samples and prepare standard solutions. More than one PDS concentration may be necessary to meet this requirement. Nominal analyte PDS may be prepared at an identical concentration for all analytes of 0.5 ng/µL. The user may modify the concentrations of the individual analytes based on the confirmed QRLs and the desired measurement range. Premixed standards containing most of the target analytes in this method may be used as a PDS. For those compounds not available in this mixture, a second source standard from the same vendor as the ICAL may be used to complete the target list compounds in the PDS. If the PDS is stored cold, warm the vials to room temperature and vortex mix prior to use.

7.3.11 Calibration Standards. Prepare a series of calibration standards of at least five levels by diluting the analyte PDS into methanolic ammonium hydroxide (1.5% v/v). The lowest calibration standard must be at or below the QRL for each analyte. The calibration standards may also be used as Continuing Calibration Checks (CCCs). Using the PDS solutions, add a constant amount of the pre-analysis standard(s) and to each calibration standard. The concentration of the pre-extraction standards should match the concentration of the analogues in sample extracts, assuming 100% recovery through the extraction process. The analyte calibration ranges from approximately 0.50 ng/mL to 25 ng/mL.

7.4 Nitrogen. 99.999 percent (ultra-high) purity used to concentrate sample extracts.

7.5 Argon. Used as collision gas in MS/MS instruments. Argon must meet or exceed instrument manufacturer's specifications. Nitrogen may be used as the collision gas if recommended by the instrument manufacturer.

8.0 Sample Collection, Recovery, Preservation, and Storage

8.1 Sampling. This method involves collection and recovery of trace concentrations of semivolatile polar organic compounds. Therefore, field sampling and recovery staff must be trained in the best practices for handling and using organic solvents in field environments to recover and protect samples from contamination.

8.1.1 Pretest Preparation.

8.1.1.1 Cleaning Glassware. Clean glassware thoroughly before using. This section provides a recommended procedure, but any protocol that consistently results in contamination-free glassware meeting the LSMB criteria in Section 9.2.2.1 of this method is acceptable.

Note: To prepare heavily soiled glassware, remove surface residuals from the glassware by soaking in hot soapy water, rinsing with hot water, then soaking with a non-chromic acid oxidizing cleaning reagent in a strong acid (e.g., NOCHROMIX® prepared according to manufacturer's directions). After the acid soak, rinse with hot water and perform the cleaning procedures in Section 8.1.1.1 of this method.

8.1.1.1.1 Soak all glassware in hot soapy water (Alconox®, Liquinox®, or equivalent) at 50 °C or higher.

8.1.1.1.2 Rinse three times with hot tap water.

8.1.1.1.3 Rinse three times with deionized/distilled water.

8.1.1.1.4 Rinse three times each with acetone, then with dichloromethane, and finally with methanol.

8.1.1.1.5 Bake glassware at 300 °C (572 °F) for a minimum of 2 hours

Note: Repeated baking of glassware may cause active sites on the glass surface that may irreversibly absorb target compounds.

8.1.1.1.6 Cover glassware openings with clean glass fitting caps or cleaned aluminum (see Section 6.2.6 of this method).

8.1.1.1.7 If exposure to glassware contamination is a concern, rinse glassware immediately prior to initial use with methanolic ammonium hydroxide (1.5% v/v). If any sampling glassware is reused for sampling without repeating the cleaning procedures in 8.1.1.1.1 through 8.1.1.1.5, the glassware must be cleaned with the rinsing solution described in Section 7.2.3 immediately before reuse.

8.1.1.2 Adsorbent Module. Load the modules in a clean area to avoid contamination. Spike modules before the sampling event, but do not spike the modules in the field. Fill a module with 20 to 40 g of XAD–2. Add the pre-sampling standard spike to the top quarter of the adsorbent bed. Add sufficient spike (picograms (pg)/module) to result in the final theoretical concentrations specified in Table 45-3 of this method. For samples with known or anticipated target compound concentration significantly higher or lower than the specified amount in these tables, add a pre-sampling spike amount appropriate to the expected native compound concentration, but no less than 10 times the detection limit. Add cleaned glass wool to the head of the XAD–2 module and tightly seal both ends of the module with appropriate size clean glass ball joint caps.

8.1.1.3 Sampling Train. Figure OTM-45-1 of this method shows the complete sampling train.

8.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air-tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container on the outside of each container. As an alternative, directly weigh the silica gel in its impinger or sampling holder just prior to sampling.

8.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container. Do not mark filters with ink or any other contaminating substance.

8.1.2 Preliminary Determinations. Use the procedures specified in Section 8.2 of Method 5 of appendix A-3 to 40 CFR part 60.

8.1.2.1 Sample Volume. This method recommends sampling enough gas volume to reach a stack sample MDL sufficient to meet test objectives. Unless otherwise specified in an applicable rule, permit, or other requirement, collect a minimum of 3.0 dry standard cubic meters of source gas.

8.1.2.2 For continuously operating processes, use the same sampling time at each traverse point. To avoid timekeeping errors, use an integer, or an integer plus one-half minute, for each traverse point.

8.1.2.3 For batch processes, determine the minimum operating cycle duration, dividing the sampling time evenly between the required numbers of traverse points. After sampling all traverse points once, sample each point again for the same duration of time per sampling point in reverse order until the operating cycle is completed. Sample all traverse points at least twice during each test run.

8.1.3 Preparation of Sampling Train. Do not use sealing greases, PTFE tape or brominated flame retardant-coated tape in assembling the train.

8.1.3.1 During field preparation and assembly of the sampling train, keep all train openings sealed where contamination can enter until just prior to assembly or until sampling is about to

begin. To protect the adsorbent module from radiant heat and sunlight, wrap the module with aluminum foil that has been rinsed with extraction solvent or wrap with other suitable material capable of shielding the module from light. The XAD–2 adsorbent resin temperature must never exceed 50 °C (122 °F) because thermal decomposition will occur.

8.1.3.2 Include at least one complete sample train proof blank sampling train per source test, as described in Sections 9.1.3 of this method.

8.1.3.3 If a sample train field blank is performed as part of a test program, recover as described in section 9.1.4 of this method.

8.1.3.4 Place approximately 100 mL of water in each of the second, third and fourth impingers but leave the first (condensate trap) impinger empty. Transfer approximately 200 g or more of silica gel from its container to the fifth impinger. Weigh each impinger and the adsorbent module, including the fitting caps, to the nearest 0.5 g using the field balance and record the weight for moisture determination. Remove the aluminum foil from the adsorbent module before weighing. Keep the module out of direct sunlight and rewrap the module with foil immediately after recording the module weight.

8.1.3.5 Using tweezers or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered, and the gasket properly placed, to prevent the sample gas stream from circumventing the filter. Check the filter for tears after completing the assembly.

8.1.3.6 Prepare the inside of the sampling probe and nozzle by brushing each component while rinsing three times each with methanol. Install the selected nozzle. You may use connecting systems described in Section 6.1.2 of this method. Mark the probe with heat resistant tape or by

some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as shown in Figure 45–1 of this method. Orient the adsorbent module vertically so condensed moisture drains into the first impinger. See APTD-0576 Maintenance, Calibration, and Operation of Isokinetic Source-sampling Equipment (U.S. EPA 1972) for details.

8.1.3.7 Turn on the recirculation pump to the adsorbent module and condenser coil and begin monitoring the temperature of the gas entering the primary adsorbent module. On commencement of sampling, ensure proper temperature of the gas entering the adsorbent module before proceeding.

8.1.4 Leak-Check Procedure. Prepare, assemble, and leak check sampling and proof blank trains. Same as Section 8.4 of Method 5 of appendix A-3 to 40 CFR part 60.

8.1.5 Sampling Train Operation. Same as Sections 8.5.1 through 8.5.9 of Method 5 of appendix A-3 to 40 CFR part 60 with the exception that the probe and filter holder (and heated sample transfer line, if used) temperature are limited to minimize the potential thermal degradation of thermally labile PFAS compounds such as HFPO-DA which are known to decompose at temperatures below the standard Method 5 probe and filter operating temperatures.

8.1.5.1 Probe and Filter Operating Temperatures – Combustion Sources. For stack temperatures at or above 120 °C, operate the probe and filter at 120 °C ± 14 °C (248 °F ± 25 °F). Monitor the filter temperature sensor and record the filter temperature during sampling. A nominal filter exit temperature of 120 °C ± 14 °C (248 °F ± 25 °F) may not be exceeded. For stack temperatures below 120 °C (248 °F), limit the probe and filter (and heated sample transfer line, if used)

temperature to approximately 10 °C (20 °F) above the sampling location stack temperature. Ensure the operating temperature is sufficient to avoid moisture condensation in the probe and filter holder.

Note: Use of cooled sampling probes is allowed to manage high temperature source sampling.

8.1.5.2 Probe and Filter Operating Temperatures – Non-Combustion Sources. For non-combustion sources, regardless of stack temperature, operate the probe and filter (and heated transfer line, if used) at no greater than 85 °C (185 °F). Monitor the filter temperature sensor and record the filter temperature during sampling. Avoid moisture condensation in the probe and filter holder if possible.

8.1.5.3 XAD-2 Adsorbent Module Temperatures. During field sampling you must record the temperature of the gas entering the XAD-2 adsorbent modules. The temperature of the gas must not exceed 20 °C (68 °F) for efficient capture of the target compounds.

8.2 Sample Recovery. Begin the cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

8.2.1 Sampling Train Recovery Preparation. Allow the probe to cool. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the sorbent module. When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe.

8.2.1.1 Conduct a post-test leak check.

8.2.1.2 Remove the probe from the train and close off both ends.

8.2.1.3 Seal off the inlet to the filter.

8.2.1.4 Remove the umbilical from the last impinger and cap the impinger.

8.2.1.5 Cap the filter-holder outlet and the inlet to the organic module.

8.2.1.6 Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section.

8.2.1.7 Cap all sorbent module openings.

8.2.1.8 Disconnect the first impinger (sorbent module knockout trap) from the impinger train inlet and cap both openings. Ground-glass caps, Teflon tape, or other inert materials such as cleaned aluminum foil (e.g., rinsed with methanolic ammonium hydroxide (1.5% v/v) may be used to seal all impinger openings.

8.2.2 Transfer and Inspection. Transfer the sampling train components to the cleanup area. This method recommends cleaning and enclosing this area to minimize the chances of losing or contaminating the sample.

8.2.2.1 To avoid sample contamination, smoking or eating in the sample recovery area shall not be allowed. Inspect the train prior to and during disassembly.

8.2.2.2 Note and record any abnormal conditions (e.g., broken filters, colored impinger liquid, etc).

8.2.3 Moisture Weight. All weights are measured and recorded with ± 0.5 g resolution using the field balance. This information is required to calculate the moisture content of the effluent gas.

8.2.3.1 Remove and weigh the primary and breakthrough adsorbent modules after removing the foil and emptying the water jacket.

8.2.3.2 Weigh the impingers.

8.2.3.3 Weigh the silica gel impinger.

Note: Moisture measurement in the field using the OTM-45 train requires weighing the primary and secondary adsorbent modules before the sampling run described in 8.1.3.2 and after sampling as part of the sample recovery for stack moisture determination.

8.2.4 Recover and prepare samples for shipping. Store all collected samples refrigerated or on ice ≤6 °C (43°F) until laboratory shipment.

8.2.4.1 Container 1 – Filter. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. If it is necessary to remove the filter, use a pair of cleaned tweezers to handle the filter. If necessary, fold the filter such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers that adhere to the filter holder gasket by using a clean, dry inert bristle brush and a clean sharp-edged blade. Seal the container and store refrigerated or on ice until laboratory shipment. .

8.2.4.2 Container 2 – Front Half Rinse. Quantitatively recover material deposited in the nozzle, the front half of the filter holder, and the cyclone, if used, by brushing while rinsing three times with methanolic ammonium hydroxide (1.5% v/v). Limit the rinse to a volume that is adequate to successfully recover the sample. Collect all the rinses in the HDPE sample bottle and label as

Container No. 2. Mark the level of the liquid on the container. Store the sample container refrigerated or on ice until laboratory shipment.

8.2.4.3 Container 3 – Use the adsorbent trap module as a sample transport container. Seal both ends with tightly fitting ground-glass stoppers followed by Teflon tape around the glass joint. Label the sorbent trap, re-cover with aluminum foil, and store refrigerated or on ice until shipment to the laboratory.

Note: The XAD-2 resin modules (primary and secondary) are shipped back from the field as separate fractions for analysis. As more data is collected from the use of this method, the requirement of analysis of the XAD-2 modules as separate fractions may change.

8.2.4.4 Container 4 – Back Half Rinse. All sampling train components located between the back half of the filter holder and the inlet of the primary adsorbent module, including the condenser if a separate condenser and adsorbent module are used, and the heated sample transfer line connecting the filter outlet to the condenser (if used) shall be triple rinsed with methanolic ammonium hydroxide (1.5% v/v). Collect all the rinses in the HDPE sample bottle and label as Container No. 4. Weigh and record the sample container weight. Store the sample container refrigerated or on ice until laboratory shipment.

8.2.4.5 Container 5 – Condensate and Impinger Water. After weighing the impingers, quantitatively recover the impinger water samples, including the contents of the knockout impinger (if used), in the HDPE sample bottle and label as Container No. 5 Mark the level of the liquid on the container. Store the sample container refrigerated or on ice until laboratory shipment.

8.2.4.6 Container 6 – Impingers Rinse. Rinse impingers 1-4 three times with methanolic ammonium hydroxide (1.5% v/v). Collect all the rinses in the HDPE sample bottle and label as Container No. 6. Mark the level of the liquid on the container. Store the sample container refrigerated or on ice until laboratory shipment.

8.2.4.7 Container 7 – Secondary Adsorbent Module Sample. Use the adsorbent trap module as a sample transport container. Seal both ends with tightly fitting ground-glass stoppers followed by Teflon tape around the glass joint. Label the sorbent trap, re-cover with aluminum foil, and store refrigerated or on ice during shipment to the laboratory.

8.2.4.8 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and report its condition on the field data sheet.

8.2.4.9 Field Sample Handling, Preservation, Storage, and Transport. Store all field samples, , temporarily refrigerated or on ice ≤6 °C (43°F) and dark conditions prior to transport to the laboratory. Ship samples on ice ≤6 °C (43°F), shielded from ultraviolet light. In addition, follow the procedures in ASTM D6911-15 (Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis) for all samples, where appropriate. To avoid contamination of the samples, pay special attention to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the adsorbent cartridges.

Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with PFAS-free paraffin wax film or PFAS free Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward.

8.2.5 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. Follow the chain of custody procedures in ASTM D4840-99 (2018)e1 (Standard Guide for Sampling Chain-of-Custody Procedures) for all samples (including field samples and blanks).

8.3 Laboratory Sample Storage Conditions and Laboratory Hold Times.

8.3.1 Table 45-4 of this method summarizes the sample storage conditions and laboratory hold times.

8.3.2 Store sampling train rinses and filter samples in the dark at 6 °C (43 °F) or less from the time the laboratory receives the samples until extraction.

8.3.3 You may store adsorbent samples prior to extraction in the dark at 6 °C (43 °F) or less for up to one year from the time the laboratory receives the samples.

8.3.4 You may store archived extracted samples in the dark at refrigerator temperature of approximately 6 °C (43 °F) for up to one year.

9.0 Quality Control

It is the testing team's responsibility to establish the conditions for optimum sample collection, extraction, cleanup, and concentration to meet the performance criteria in this method. However, you may not change the fundamental procedures of isokinetic sampling with an adsorbent collection media followed by sample extraction, and LC-MS/MS with isotopic dilution quantification. This method requires performing a LSMB assessment to evaluate an individual laboratory's performance against the performance criteria in this method.

In recognition of advances that are occurring in sampling and analytical technology for PFAS measurement, and to allow the test team to overcome analyte sensitivity and matrix interferences, this method allows certain options to increase sample collection volume and to improve separations and the quality of the analysis results for target analytes.

Quality control (QC) procedures include the Initial Demonstration of Capability (IDC) and ongoing QC requirements. This section describes each QC parameter, its required frequency, and the performance criteria that must be met to satisfy method objectives. The analysis QC criteria discussed in the following sections are summarized in Table 45-5. These QC requirements are considered the minimum for an acceptable QC program. Laboratories are encouraged to institute additional QC practices to meet their specific needs. At a minimum, laboratories must evaluate changes within the alternatives allowed in this method using a media blank sample to re-demonstrate that the performance criteria are achieved.

9.1 Sampling Quality Control.

9.1.1 Sampling System. Same as Sections 9 in SW 846 Method 0010.

9.1.2 Field Sample Media Blank (FSMB). Also called the field trip blank. The FSMB is intended to include and represent the sampling media (i.e., filter, XAD-2 adsorbent) and reagents (i.e., impinger contents, rinsing solvents) associated with the field sample collection and recovery, but is not actually used in the field. The FSMB is treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, and all analytical procedures. The purpose of the FSMB is to determine if method analytes or other interferences are introduced into the sample from shipping, storage, and the field environment. Compare the

analysis results of the FSMBs to the background level criteria in 9.2.2.1 and associated Table 45-5. Failure to meet these levels does not invalidate data. However, the measured target compound mass in each fraction of the FSMB will need to be reported so they may be used to interpret sample results.

Note: If Teflon tape is used, the FSMB shall include background level determination. A representative length (e.g., 20ft) shall be extracted and analyzed with the results compared to the background level criteria in 9.2.2.1.

9.1.3 Sample Train Proof Blank (STPB). A STPB must be submitted with the samples collected at each sampling site. At a minimum, conduct at least one STPB for each test series at a sampling site. A STPB consists of a fully assembled train at the sampling site using glassware that has been cleaned, but not yet used for sampling. Prepare and assemble the STPB in a manner identical to that described in Section 8.1.3 and 8.1.4 of this method. The STPB is taken to the sampling area, and leak checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. No gaseous sample will be passed through the sampling train. Recover the STPB as an actual train described in Section 8.2 of this method. Follow all subsequent steps used for actual field train samples, including sample preparation, analysis, and data reporting. Table 45-5 of this method includes the performance criteria for the STPB samples. Failure to meet these performance levels does not invalidate data. However, the measured target compound mass in each fraction will need to be reported and so they may be used to interpret sample results.

9.1.4 Optional Sample Train Field Blank. STFB may be performed and submitted with the samples collected at each sampling site. STFB are performed to demonstrate complete recovery of samples from used sampling systems before recycling the glassware for an additional run. A STFB train consists of a fully assembled train at the sampling site using glassware that has been previously used for sampling. Prepare and assemble the blank train in a manner identical to that described in Section 8.1.3 and 8.1.4 of this method. The STFB train is taken to the sampling area and leak checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. No gaseous sample will be passed through the sampling train. The train will be recovered as if it were an actual test sample. Recover the field blank train as an actual train described in Section 8.2 of this method. Follow all subsequent steps for blank train sample preparation and analysis used for field train samples, including data reporting. Table 45-5 of this method includes the performance criteria expected for field train blank samples. Failure to meet these levels does not invalidate data. However, the measured target compound mass in each fraction may be reported for use in interpreting sample results.

9.1.5 Pre-sampling Standard Retention. Pre-sampling standard spike results must demonstrate acceptable recovery in the first three fractions of the sampling train. Results outside of the acceptable range (Table 45-5) of 70-130% for the pre-sampling standard spikes may require an evaluation for the cause of the poor sampling retention. Significant accumulation of pre-sampling standards in the breakthrough sorbent trap is an indication of poor target sample retention. If the pre-sampling standard recovery in the combined results from the first three fractions is less than 50%, the data for that train are not considered valid subject to data user evaluation to determine fit for purpose.

Note: The pre-sampling standard recoveries include the sum of the analytical results of Fractions 2 and 3 because the pre-sampling standard may have migrated from the XAD-2 into the impingers.

9.1.6 Secondary XAD-2 Breakthrough. Determine the relative breakthrough (BT) of PFAS through the OTM-45 train. For each PFAS target compound, calculate breakthrough.

$$BT(\%) = \frac{(Fraction\ 4\ mass)}{(Fraction\ 1{+}2{+}3\ mass)}\ x\ 100\% \qquad \text{Eq. 45-3}$$

For any BT greater than 10%, add the Fraction 4 mass to the total sample mass for emissions calculations and flag the associated data. The BT calculation is not required when the fraction 4 target compound mass is below three times its MDL..

Note: At low (at or near the QRL) fractions 1-3 mass totals, the calculated BT may be biased high relative to fraction 4 mass levels, e.g., if background contamination of the breakthrough trap occurs. In these instances where the calculated BT exceeds 10% and each of fractions 1-3 are less than the QRL, do not add the fraction 4 mass to the fraction 1-3 mass totals. Flag the associated data and assess impact on results.

9.2 Analysis Quality Control.

9.2.1 Initial Demonstration of Capability (IDC). The IDC must be successfully performed prior to analyzing field samples by meeting the QC requirements in Table 45-6. The IDC must be repeated if changes are made to analytical parameters not previously validated during the IDC. This may include, for example, changing the sample volume, selecting alternate quantitation ions, extending the calibration range, adding additional pre-analysis standard(s), or adding

additional pre-extraction standards. Prior to conducting the IDC, the analyst must meet the calibration requirements outlined in Section 10. The same calibration range used during the IDC must be used for the analysis of field samples.

9.2.1.1 Perform initial calibration following the procedures in Section 10.4 The lowest calibration standard used to establish the initial calibration (as well as the low-level CCC) must be within two to ten times the MDL.

9.2.1.2 Demonstration of Low System Background. Analyze an LSMB immediately after injecting the highest calibration standard in the selected calibration range. Confirm that the LSMB is free from contamination as defined in Section 9.2.2.1. If an automated extraction system is used, an LSMB must be extracted on each port to fulfill this requirement.

9.2.1.3 Initial MDL Determination. Perform an MDL determination for each sample fraction (front half rinse and filter, XAD-2, and impinger solution) following the requirements in 40 CFR Part 136 Appendix B. The MDL determination includes seven LSMB and seven LFMB that are prepared from blank media, spiked within 2 to 10 times of the expected MDL, and processed in a manner identical to field sample preparation. The MDL study establishes the lowest detectable concentrations for each sampling train fraction. Sample specific MDLs are reported inclusive of sample-specific dilutions, final volumes, aliquots, etc.

9.2.1.4 MDL Confirmation. Prepare a LSMB for each sampling medium by spiking each medium with native target compounds at the MDL and pre-extraction isotopic labeled standards at the concentration used to analyze field samples. Prepare and analyze the spiked LSMB and

confirm target compounds meet the qualitative identification criteria in Section 12.3.2 of this method.

9.2.1.5 Demonstration of Precision. Prepare, extract, and analyze seven replicate LFMBs in a valid Extraction Batch (seven LFMBs and an LSMB). Fortify the LFMBs near the midpoint of the initial calibration curve. The percent relative standard deviation (RSD) of the concentrations from the replicate analyses must be ≤ 20% for all method analytes.

9.2.1.6 Demonstration of Accuracy. Using the same set of replicate data generated for Section 9.2.1.5, calculate the average percent recovery. The average recovery for each analyte must be within a range of 70–130%.

9.2.1.7 Lowest Calibration Concentration Confirmation. Establish a target concentration for the lowest calibration standard based on the intended use of the method. The lowest calibration concentration may be established by a laboratory for their specific purpose or may be set by a regulatory agency. If there is a regulatory or programmatic lowest quantitative reporting requirement, the laboratory calibration curve must be set at or below this level. In doing so, one should consider that establishing the lowest calibration concentration too low may cause repeated failure of ongoing QC requirements in Section 9.2.2.

9.2.1.7.1 Prepare and Analyze LFMB Samples. Fortify, extract, and analyze seven replicate LFMBs at the proposed lowest calibration concentration.

9.2.1.7.2 Calculate Lowest Calibration Statistics. Calculate the mean and standard deviation for each analyte in these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the following equation:

$$HR_{PIR} = 3.963S \qquad \text{Eq. 45-4}$$

Where,

S = the standard deviation

3.963 is a constant value for seven replicates.[9]

9.2.1.7.3 Calculate the Upper and Lower Limits for the Prediction Interval of Results (PIR = Mean ± HR_{PIR}) as shown below. These equations are only defined for seven replicate samples.

$$U_{PIR} = \left[\frac{(Mean + HR_{pir})}{Fortified\ Concentration}\right] 100\% \qquad \text{Eq. 45-5}$$

$$L_{PIR} = \left[\frac{(Mean - HR_{pir})}{Fortified\ Concentration}\right] 100\% \qquad \text{Eq. 45-6}$$

9.2.1.7.4 Lowest Calibration Point Acceptance Criteria. The laboratory's ability to measure analyte concentrations down to the lowest calibration point is confirmed if the Upper PIR Limit is less than, or equal to, 150%; and the Lower PIR Limit is greater than, or equal to, 50%. If these criteria are not met, the lowest calibration point has been set too low and must be confirmed again at a higher concentration.

9.2.1.8 Calibration Verification. Analyze a QCS to confirm the accuracy of the primary calibration standards. Results must be within 70-130% of the true value.

9.2.2 Ongoing QC Requirements. This section describes the ongoing QC elements that must be included when processing and analyzing field samples.

9.2.2.1 Blanks and Background Levels. The quantitative measurement of various blanks and sampling media background levels is required. Unless otherwise stated, estimated quantitative

measurement, and therefore acceptable blank and background levels for these samples should be at or below the MDLs determined using the procedure described in Section 9.2.1.3. Ideally, estimated quantitative limits, and therefore acceptable blank and background levels, should be at or below the established MDLs, but no greater than the MDL. Sample results are flagged if blank media or proof train blanks exceed three times the MDL. Data users must consider blank results to determine if sample results are fit for purpose.

9.2.2.1.1 Sampling Media Background Level Checks. When performing cleanliness checks prior to field sampling on the sampling media (i.e., filters, XAD-2, reagents, solvents, etc.), acceptable levels should be at or below three times the established MDLs. If sampling media blank concentrations are found above three times the MDL, you must clean the sampling media until levels are below this criterion.

9.2.2.1.2 Laboratory Sample Media Blank (LSMB). Analyze at least one LSMB during an analytical sequence or every 24 hours, whichever is shorter. Sampling media and reagents are fortified with the pre-extraction standards and processed identically to a field sample of the same media. LSMBs for each sampling media and reagent (i.e., filter, XAD-2, water, rinsing solutions) are included in each Extraction Batch to determine if the method analytes or other interferences are introduced from the laboratory environment, the reagents, glassware, or extraction apparatus. Acceptable levels should be at or below three times the MDLs. If method analytes are detected in the LSMB at concentrations greater than or equal to this level the results must be flagged accordingly. Identify and correct the source of contamination if LSMB are analyzed prior to a sampling event before proceeding with additional analyses. Compare LSMB to STPB results and provide QC narrative explanation of the impact of LSMB and STPB on field sample results.

9.2.2.2 Estimating Background Concentrations. Although data below the lowest calibration concentration may not be accurate enough for quantitative data reporting, such data are useful in determining the magnitude of background interference. Therefore, the analyte concentrations in the LSMB may be estimated by extrapolation when results are below the lowest calibration concentration.

9.2.2.2.1 Influence of Background on Selection of MDLs. Because media and field blank contamination can be significant, detection limits are both instrument sensitivity and blank limited. Results at or below the LSMB or STPB must be flagged as blank limited results.

9.2.2.2.2 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 LSMBs must be analyzed (to detect potential carryover) until the system meets the LSMB 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 MDL, these samples are invalid. If the affected analytes do not exceed the MDL, these subsequent samples may be reported.

9.2.2.3 Calibration Acceptance Criteria. Evaluate the initial calibration by calculating the concentration of each analyte as an unknown against its regression equation (see Section 10.4). For calibration levels, the result for each analyte should be within 90 – 110% of their true value. If these criteria cannot be met, the analyst may have difficulty meeting ongoing QC criteria. In this case, corrective action is recommended such as reanalyzing the calibration standards, restricting the range of calibration, or performing instrument maintenance. If the cause for failure

to meet the criteria is due to contamination or standard degradation, prepare fresh calibration standards and repeat the initial calibration.

9.2.2.3.1 Continuing Calibration Check (CCC). Analyze CCC standards at the beginning of each Analysis Batch, after every tenth field sample, and at the end of the Analysis Batch (see Section 10.5). CCCs must be within 70-130% of the true value. If the CCC fails because the concentration is >130% (150% for low-level CCC) and field sample extracts show no concentrations above the MDL for that analyte, non-detects can be reported without re-analysis.

9.2.2.4 Laboratory Fortified Media Blanks (LFMB). Duplicate low level and high level LFMBs are required with each extraction batch for each media fraction (i.e., filter, XAD-2, water).

9.2.2.4.1 LFMB Concentration Requirements. Fortify the low concentration LFMB no more than two times the lowest calibration point. Fortify the high level LFMBs at a concentration between the mid and high-level calibration points.

9.2.2.5 Pre-analysis Standard(s) Areas. The analyst must monitor the peak areas of the pre-analysis standard(s) in all injections of the Analysis Batch. The pre-analysis standard(s) in any chromatographic run must be within 50–150% of the average area measured during the initial calibration. Random evaporation losses have been observed with the polypropylene caps causing high-biased pre-analysis standard(s) areas. If a pre-analysis standard(s) area for a single sample in an analysis batch does not meet these criteria, reanalyze the extract in a subsequent analysis batch. If the pre-analysis standard(s) area fails to meet the acceptance criteria in the repeat analysis, or if multiple samples in a batch fail to meet the pre-analysis spike criteria, perform corrective action, and reanalyze the failed samples.

9.2.2.6 Pre-extraction Standard Recoveries. Pre-extraction standard recoveries determined during the analysis of samples must demonstrate on a per sample basis that recovery of the labeled standard achieved the 20-200% recovery requirements summarized in Table 45-5. Calculate the percent recovery (%R) for each analogue as follows:

$$\%R = \frac{Measured\ Concentration\ of\ the\ Pre{-}extraction\ Isotope\ analogue}{Fortification\ concentration\ of\ the\ Pre{-}extraction\ Isotope\ analogue}\ x\ 100 \qquad \text{Eq. 45-7}$$

Recoveries below the acceptable range for pre-extraction spikes are an indication that sample preparation procedures did not adequately address sample and or sample matrix processing to recover native target compounds. Compounds that fail this criterion must be flagged and reported as not quantitative because of QC failure. Such failure may require a repeated field sampling effort.

9.2.2.7 Evaluate Analyte Recovery. Calculate the LFSM native compound percent recovery (%R) using the following equation:

$$\%R = \frac{(A-B)}{C}\ x\ 100 \qquad \text{Eq. 45-8}$$

Where,

A = measured concentration in the fortified sample,

B = measured concentration in the unfortified sample, and

C = fortification concentration.

Note: To obtain meaningful percent recovery results, correct the measured values in the LFSM and LFSMD for the native levels in the unfortified samples, even if the native values are less than the lowest calibration concentration.

Results for analytes fortified at concentrations near or at the lowest calibration point (within a factor of two times the lowest calibration concentration) must be within 50–150% of the true value. Results for analytes fortified at higher concentrations must be within 70–130% of the true value. If the LFMB results do not meet these criteria, then report all data for the problem analytes in the Extraction Batch with a note that the LFMB accuracy criteria were not met. The laboratory must investigate the root cause for this failure and report their findings and corrective action.

9.2.2.8 Calibration Verification using QCS. A QCS must be analyzed during the IDC and then quarterly thereafter. For this method, the laboratory is not required to obtain standards from a source independent of the primary calibration standards. Instead, the laboratory should acquire the best available quantitative standards and use these to prepare both the primary calibration standards and the QCS. The QCS must be an independent dilution beginning with the common starting materials. Preparation by a second analyst is recommended. The acceptance criterion for the QCS is 70–130% of the true value. If the accuracy for any analyte fails the acceptance criterion, prepare fresh standard dilutions, and repeat the Calibration Verification.

9.3 Analysis Method Modification QC Requirements.

The analyst is permitted to modify the chromatographic and MS/MS conditions. Examples of permissible method modifications include alternate LC columns, MRM transitions, and

additional QC analytes proposed for use with the method. Any method modifications must be within the scope of the established method flexibility and must retain the basic chromatographic elements of this method. The following are required after a method modification.

9.3.1 Repeat the IDC. Establish an acceptable initial calibration using the modified conditions. Repeat the procedures of the IDC.

9.3.2 Document Performance in Representative Sample Matrices. The analyst is also required to evaluate and document method performance for the modifications in an archived field sample treated as a matrix spike.

9.4 Record and Report Requirements.

Record and report data and information that will allow an independent reviewer to validate the determination of each target compound concentration. At a minimum, record and report the data as described in Sections 9.4.1 through 9.4.7 of this method.

9.4.1 Facility and facility location.

9.4.2 Field sampling company and sampling team members.

9.4.3 Field sampling date.

9.4.4 Field sample volume.

9.4.5 Field quality check results.

9.4.6 Analysis laboratory.

9.4.7 Sample numbers and other sample identifiers. Each sample must have a unique identifier.

9.4.8 Extraction dates.

9.4.9 Analysis dates and times.

9.4.10 Analysis sequence/run chronology.

9.4.11 Quantitation Reports. The end data user has the responsibility to decide how and if the data is fit for purpose, so they will need to have access to both the individual fraction results and the sampling train sum. Sampling train results are reported as the sum of the first three fractions and separately for the secondary module. Individual compound results are reported for each fraction.

9.4.12 Laboratory quality narrative on any issues or QC excursions, including the results of how the analyses met or failed performance requirements.

9.4.13 Identity and location of the raw field sampling and raw analytical data storage.

9.5 Reporting and Flagging Sampling Train Fraction Sums.

9.5.1 When an OTM-45 sampling train combined result has data where each fraction has detected amounts of a target compound, the data are reported as the sum and flagged ADL (above detection limit).

9.5.2 When an OTM-45 sampling train combined result has data where all fractions were at or below the detection limit for a target compound, the data are reported as the sum of the detection limits and flagged BDL (below detection limit).

9.5.3 When an OTM-45 sampling train combined result has data where one or two fractions were below detection limit and one fraction is above the detection limit, the data are reported as the sum of the detection limits and the above detection limits and flagged as DLL (detection level limited).

10.0 Calibration and Standardization

10.1 Sampling System. Same as Sections 9 in SW 846 Method 0010.

10.2 MS/MS Optimization.

10.2.1 MS Parameters. Instrumental parameters are optimized for the precursor and product ions listed in Table 45-2. Product ions other than those listed may be selected; however, the analyst should avoid using ions with lower mass or common ions that may not provide enough discrimination between the analytes of interest and co-eluting interferences.

10.2.2 Precursor Ion. Optimize the response of the precursor ion ([M – H]– or [M – CO_2 – H]–) for each analyte following the instrument manufacturer's guidance. Optimization may be performed at analyte concentrations of 1.0 μg/mL. Vary the MS parameters (source voltages, source and desolvation temperatures, gas flows, etc.) until optimal analyte responses are determined. The analytes may have different optimal parameters, requiring some compromise on the final operating conditions.

10.2.3 Product Ion. Optimize the product ion for each analyte following the instrument manufacturer's guidance. Typically, the carboxylic acids have similar MS/MS conditions, and the sulfonic acids have similar MS/MS conditions.

10.3 Chromatographic Conditions. Establish LC operating parameters that optimize resolution and peak shape. Example LC starting conditions can be found in Table 45-7. Modifying the solvent composition of the standard or extract by increasing the aqueous content to better focus early eluting compounds on the column is not permitted. A decrease in methanol concentration could lead to lower or imprecise recovery of the more hydrophobic method analytes, while higher methanol concentration could lead to the precipitation of salts in some extracts. The peak shape of the early eluting compounds may be improved by increasing the volume of the injection loop or increasing the aqueous content of the initial mobile phase composition.

10.3.1 Minimizing PFAS Background. LC system components, as well as the mobile phase constituents, may contain many of the analytes in this method. These PFAS may 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.

10.3.2 Establishing Branched vs. Linear Isomer Profiles. Prepare and analyze the technical-grade standard of PFOA at a mid- to high-level concentration. Identify the retention times of the branched isomers of PFOA present in the technical-grade PFOA standard. When PFOA is chromatographed on a reversed-phase column, the branched isomers elute prior to the linear isomer. Repeat the procedure in this section for technical grade PFHxS and PFOS, and any other analytes for which technical-grade standards have been acquired. The branched isomer

identification checks must be repeated any time chromatographic changes occur that alter analyte retention times.

10.3.3 Establish LC-MS/MS Retention Times and MRM Segments. Inject a mid- to high-level calibration standard under optimized LC-MS/MS conditions to obtain the retention times of each method analyte. Divide the chromatogram into segments that contain one or more chromatographic peaks. For maximum sensitivity, minimize the number of MRM transitions that are simultaneously monitored within each segment. Both primary and secondary product ions may need to be monitored to quantitate selected PFAS. Ensure that the retention time window used to collect data for each analyte is of sufficient width to detect earlier eluting branched isomers.

10.4 Initial Calibration. This method has four pre-analysis standard(s) that are used to determine recoveries of the isotopically-labeled pre-extraction standards. The pre-extraction standards are used as isotope dilution or extracted internal standards to quantify the native analyte concentrations. The pre-extraction quantification reference compounds for the native analytes are listed in Table 45-1.

10.4.1 Calibration Standards. Prepare a set of at least five calibration standards as described in Section 7.4.11. The analyte concentrations in the lowest calibration standard must be within three to ten times the MDL. Suggested calibration standard concentrations for native target compounds are shown in Table 45-8. Suggested calibration standard concentrations for pre-extraction isotopic labeled compounds are shown in Table 45-9.

10.4.2 Calibration Curves of Native Analytes. Quantitate the native analytes using the internal standard calibration technique. The internal standard technique calculates concentration based on the ratio of the peak area of the native analyte to that of the isotope dilution analogue. Calibrate the LC-MS/MS and fit the calibration points with either a linear or quadratic regression. Weighting may be used.

Note: Optional forcing the calibration curve through the origin may improve the estimate of the background levels of method analytes.

Note: The MS/MS instrument used during method development was calibrated using weighted (1/x) quadratic regression with forced zero.

10.4.3 Calibration of Pre-extraction Standards. The pre-extraction standards are quantified using the pre-analysis calibration technique. Because these isotopes are added at a single concentration to the calibration standards, calibrate for each of these using an average response factor.

10.4.4 Calibration of Pre-analysis Standard(s). Because pre-analysis standard(s) are added at a single concentration to the calibration standards, calibrate for each of these using an average response factor.

10.4.5 Calibration Acceptance Criteria. Evaluate the initial calibration by calculating the concentration of each analyte as an unknown against its regression equation. All calibration points should be within 90 – 110% of their true value. If these criteria cannot be met, the analyst could have difficulty meeting ongoing QC criteria. In this case, corrective action is recommended such as reanalyzing the calibration standards, restricting the range of calibration, or performing instrument maintenance. If the cause for failure to meet the criteria is due to

contamination or standard degradation, prepare fresh calibration standards and repeat the initial calibration.

10.5 Continuing Calibration. Analyze a CCC to verify the initial calibration at the beginning of each analysis batch, after every tenth field sample, and at the end of each Analysis Batch. The beginning CCC for each Analysis Batch must be at, or below, the QRL for each analyte. This CCC verifies instrument sensitivity prior to the analysis of samples. If standards have been prepared such that all low calibration levels are not in the same solution, it may be necessary to analyze two standards to meet this requirement. Alternatively, the nominal analyte concentrations in the analyte PDS may be customized to meet these criteria. Alternate subsequent CCCs between the mid and high calibration levels. Verify that the CCC meets the criteria in the following sections.

10.5.1 CCC- Pre-analysis Standard(s) Responses. The absolute area of the quantitation ion for each of the pre-analysis standard(s) must be within 50–150% of the average area measured during the initial calibration. If these limits are exceeded, corrective action is necessary (Section 10.5).

10.5.2 CCC Isotope Dilution Analogue Recovery. Using the average response factor determined during the initial calibration and the internal standard calibration technique, calculate the percent recovery of each isotope dilution analogue in the CCC. The recovery for each analogue must be within a range of 70–130%. If these limits are exceeded, corrective action is necessary (Section 10.5).

10.5.3 CCC Analyte Responses. Calculate the concentration of each method analyte in the CCC. Each analyte fortified at a level less than or equal to the QRL must be within 50–150% of the true value. The concentration of the analytes in CCCs fortified at all other levels must be within 70–130%. If these limits are exceeded, then all data for the failed analytes must be considered invalid. Any field samples analyzed since the last acceptable CCC that are still within holding time must be reanalyzed after an acceptable calibration has been restored.

10.5.3.1 Exception for High Recovery. If the CCC fails because the calculated concentration is greater than 130% (150% for the low-level CCC) for a method analyte, and field sample extracts show no concentrations above the MDL for that analyte, non-detects may be reported without re-analysis.

10.6 Corrective Action. Failure to meet the CCC QC performance criteria requires corrective action. Following a minor remedial action, such as servicing the autosampler or flushing the column, check the calibration with a mid-level CCC and a CCC at the QRL, or recalibrate according to Section 10.4 of this method. If pre-analysis standard(s) and calibration failures persist, maintenance may be required, such as servicing the LC-MS/MS system or replacing the LC column. These latter measures constitute major maintenance, and the analyst must return to the initial calibration step.

10.7 Calibration Range Flexibility. The calibration ranges for native PFAS target compounds in Tables 45-8 are provided as an example. Calibration solutions are prepared by diluting the appropriate amounts of calibration stock solutions in basic methanol extraction solution. The actual ICAL concentration used for each sample batch will depend upon the quantitation limit requirements of the program. The concentration of pre-extraction isotopically labeled

compounds used for isotopic dilution quantitation are kept constant and will depend upon the quantitation limit requirements of the test program.

11.0 Analysis Procedure

11.1 Sample Extraction. The OTM-45 sampling train (Figure 45-1) currently results in seven (7) containers that are extracted and analyzed as four (4) discrete analytical fractions. Figure OTM-45-3 provides a flow chart showing how the respective sample containers are combined, extracted, and concentrated for analysis.

11.1.1 Fraction 1 Particulate Filter and Front Half Rinse (Containers 1 and 2).

11.1.1.1 Place the particulate filter into an appropriate size HDPE bottle. Spike the filter with the appropriate pre-extraction recovery standard solution. Avoid saturation and runoff of the spike from the filter.

11.1.1.2 Add front-half sample rinsate (Container 2) to each respective filter extraction container. If there is less than 50 mL of rinsate, add methanolic ammonium hydroxide (1.5% v/v) for a total of 50 mL.

11.1.1.3 Extract samples on a shaker table for 18 hours. Measure and record the final volume.

Note: OTM-45 is a performance-based method. Extraction times less than 18 hours may be acceptable if isotopic labeled standard recovery meets the performance criteria in Section 9.

11.1.1.4 After extraction, the methanolic ammonium hydroxide (1.5% v/v) extraction solvent is divided: half of the volume used in the extraction is analyzed; the remaining portion is archived.

Filter the sample into separate, appropriately sized HDPE containers by placing a filter paper in a disposable polypropylene funnel, dampening the filter with MeOH, and pouring the sample extracts through the funnels and into the HDPE containers. Rinse each filter paper and funnel with MeOH into its sample container to recover residual target or isotopic labeled compounds.

11.1.2 Fraction 2 Primary XAD-2 Adsorbent and Back-Half Rinse (Containers 3 and 4).

11.1.2.1 Spike the XAD-2 through the glass wool plug into the sorbent bed in the module with the appropriate pre-extraction recovery standard solution (Table 45-3). Empty the module contents, including the glass wool plug, into an HDPE wide mouth bottle. Rinse the inside of the module with methanolic ammonium hydroxide (1.5% v/v) and add to the HDPE bottle.

11.1.2.2 Add up to 180 mL of the back-half sample rinsate (Container 4) to the respective XAD container. If there is less than 180 mL of rinsate, add methanolic ammonium hydroxide (1.5% v/v) for a total of 180 mL. If there is excess rinsate, (more than 180 mL), reserve the excess for a second extraction described in 11.1.2.5.

11.1.2.3 Extract the samples on a shaker table for 18 hours.

Note: OTM-45 is a performance-based method. Extraction times less than 18 hours may be acceptable if isotopic labeled standard recovery meets the performance criteria in Section 9.

11.1.2.4 After allowing the XAD-2 to settle, decant the methanolic ammonium hydroxide (1.5% v/v) extraction solvent into a new HDPE container, leaving the XAD-2 in the extraction container.

11.1.2.5 Add any unused rinsate to the XAD- HDPE extraction container. If there is less than 180 mL of back-half rinsate available for the second extraction, add methanolic ammonium hydroxide (1.5% v/v) for a total of 180 mL. Extract the sample a second time on a shaker table for a minimum of 18 hours.

11.1.2.6 After allowing the XAD-2 to settle, decant the methanolic ammonium hydroxide (1.5% v/v) extraction solvent into the container with the first extract, leaving the XAD-2 in the extraction container. Measure and record the final volume of the extract. If there are less than 360 mL of sample rinsate in the extraction container add extraction solvent for a total of 360 mL. Divide the extract, taking 90 mL of the volume for SPE concentration and archive the remaining portion.

11.1.2.7 Bring the 90 mL fraction up to 1 L using DI water and add acetic acid until a pH between 6-7 is reached. Concentrate using solid phase extraction (Section 11.2.2).

11.1.3 Fraction 3 Condensate/Impinger Water and Impinger Rinses (Containers 5 and 6).

11.1.3.1 Bring the sample (Container 5) up to 500 mL in a HDPE bottle with DI water. If the amount of sample is more than 500 mL, the entire sample is prepared (no additional DI water is added).

11.1.3.2 Spike each sample with 1.0 mL of the pre-extraction recovery standard solution.

11.1.3.3 The water sample is divided taking half of the water sample for concentration in a 1 L HDPE bottle; the remaining half is archived in an appropriately sized HDPE bottle separate from the impinger rinsate archive fraction.

11.1.3.4 The impinger rinsate (Container 6) is divided taking half of the rinse and adding it to the 1 L HDPE bottle containing half of the impinger water; the remaining half is archived in an appropriately sized HDPE bottle separate from the impinger archive fraction.

11.1.3.5 Bring the combined impinger water/rinsate up to 1 L using DI water and add acetic acid until a pH between 6-7 is reached. Concentrate using solid phase extraction (Section 11.2.2).

11.1.4 Fraction 4 Secondary XAD-2 Adsorbent (Container 7).

11.1.4.1 Spike the XAD-2 in the module with the appropriate pre-extraction recovery standard solution. Empty the module contents into an HDPE wide mouth bottle. Rinse the module with methanolic ammonium hydroxide (1.5% v/v) and add to HDPE bottle.

11.1.4.2 Add 180 mL of methanolic ammonium hydroxide (1.5% v/v) to the HDPE wide mouth bottle containing the spiked XAD-2.

11.1.4.3 Extract the sample on a shaker table for 18 hours.

Note: OTM-45 is a performance-based method. Extraction times less than 18 hours may be acceptable if Pre-extraction standard recovery meets the performance criteria in Section 9.

11.1.4.4 After allowing the XAD-2 to settle, decant the methanolic ammonium hydroxide (1.5% v/v) extraction solvent into a clean HDPE container, leaving the XAD-2 in the extraction container.

11.1.4.5 Add 180 mL of methanolic ammonium hydroxide (1.5% v/v) to the XAD extraction container.

11.1.4.6 Extract the sample a second time on a shaker table for a minimum of 18 hours.

11.1.4.7 After the second extraction is completed, decant the extraction solvent into the container with the first extract.

11.1.4.8 Measure and record the final volume of the extract. If there are less than 360 mL of sample rinsate in the extraction container add methanolic ammonium hydroxide (1.5% v/v) for a total of 360 mL. Divide the extract, taking 90 mL of the volume for SPE concentration and archive the remaining portion.

11.1.4.9 Bring the 90 mL fraction up to 1 L using DI water and add acetic acid to samples until a pH between 6-7 is reached. Concentrate using solid phase extraction (Section 11.2.2).

11.2 Sample Concentration.

11.2.1 Hot Block Concentration for Fraction 1 Extract.

11.2.1.1 Pour extract into a polypropylene digestion vessel and insert into a digestion block heated between 55-60 °C. Rinse container three times with small portions of methanolic ammonium hydroxide (1.5% v/v) and add to digestion vessel. Cover each vessel with a ribbed polypropylene watch glass.

Note: The total volume of the extract and rinsate may exceed the capacity of the digestion vessel. To accommodate larger volumes, the extract and rinsate can either be concentrated separately to a level that allows recombination (with proper rinsing) OR additional extract can be added to a digestion vessel as the volume is reduced during the concentration step.

11.2.1.2 Concentrate the sample to below 10 mL, but not to dryness. Transfer to a 10 mL polypropylene tube, rinsing the digestion vessel adequately with extraction solution.

11.2.1.3 Blow down remaining volume to below 2 mL, but not to dryness with an N-EVAP at 55-60 °C. Bring volume up to 2 mL with DI water or methanolic ammonium hydroxide (1.5% v/v). Cap snugly and ensure there are no leaks. Store refrigerated at approximately 4 °C until analysis. Analyze within 28 days of extracting.

Note: The Hot Block Concentration procedure may be replaced with Solid Phase Extraction provided the method performance criteria in Section 9 are met. Care must be taken that the capacity (organic composition and hydroxyl) of the SPE cartridge is not exceeded. See the OTM-45 FAQ for additional information.

11.2.2 Solid Phase Extraction (SPE). **The following SPE approach is intended to provide a detailed methodology known to successfully meet OTM-45 performance criteria. Because OTM-45 is a performance-based method, other approaches may be utilized provided they meet OTM-45 performance criteria in Section 9 of this method.**

11.2.2.1 Condition the SPE cartridges (Phenomenex Strata PFAS WAX/GCB, 500mg/50mg/6cc, or equivalent) by passing the following without drying the column.

11.2.2.2 Wash with 5.0 mL of methanolic ammonium hydroxide (1% v/v).

11.2.2.3 Wash with 5.0 mL of DI water. Close valve when ~ 200 µL remains on top to keep column wet.

11.2.2.4 Add samples to the columns and with vacuum, pull the entire sample through the cartridge at a rate of approximately 10-15 mL/min.

11.2.2.5 After the sample has been loaded onto the column, rinse the sample bottle with two 5 mL aliquots of reagent water and pour onto the column reservoir.

11.2.2.6 After the final loading of the sample but before completely passed through the column, rinse the SPE column with 1 mL of water.

11.2.2.7 After the sample and water rinse have completely passed through the cartridge, allow the cartridge to purge for 1 min.

11.2.2.8 Rinse the sample container with 5 mL of 30:70 methanol:water and load onto the cartridge to soak for five minutes and then elute to waste. Rinse the sample container with a second 5 mL of 30:70 methanol:water and elute to waste. Allow the column to dry with vacuum for 5 to 10 minutes.

11.2.2.9 Rinse the sample container with 4 mL of methanolic ammonium hydroxide (1% v/v) and load onto the cartridge. Allow the solution to soak for 5 minutes and then elute into polypropylene collection tubes. Repeat container rinse and cartridge elution with a second 4 mL aliquot of methanolic ammonium hydroxide (1% v/v) (without a soaking period), resulting in a total collection volume of approximately 8 mL.

11.2.2.10 Add 0.25 mL of pre-analysis standard solution (Table 45-3) at 50 ng/mL and bring the sample volume up to 10.0 ml with water for a final solvent composition of 80:20

methanol:water. Cap snugly and ensure there are no leaks. Store refrigerated at approximately 4 °C until analysis. Analyze within 28 days of extracting.

Note: Additional concentration of the methanolic SPE extract may be performed if desired, but pre-analysis standards and water/methanol additions must be proportionally adjusted to result in the final solvent composition of 80:20 methanol:water.

Note: Water and methanol do not form an azeotrope and nitrogen concentration will disproportionally remove methanol before water.

11.3 Sample Analysis.

Note: Sample analysis for this method is fashioned after EPA's Method 533 with modifications to accommodate the various fractions recovered from the stationary source sampling train.

11.3.1 Establish LC-MS/MS Operating Conditions. Establish MS/MS operating conditions per the procedures in Section 10.2 and chromatographic conditions per Section 10.3. Establish a valid initial calibration following the procedures in Section 10.3 or confirm that the existing calibration is still valid by analyzing a low-level CCC. If establishing an initial calibration for the first time, complete the IDC prior to analyzing field samples. Analyze field and QC samples in a properly sequenced Analysis Batch as described in Section 11.4.

11.3.2 Verify Retention Time Windows. The analyst must ensure that each method analyte elutes entirely within the assigned window during each Analysis Batch. Make this observation by viewing the quantitation ion for each analyte in the CCCs analyzed during an Analysis Batch. If an analyte peak drifts out of the assigned window, then data for that analyte is invalid in all

injections acquired since the last valid CCC. In addition, all peaks representing multiple isomers of an analyte must elute entirely within the same MRM window.

11.4 Analysis Batch Sequence. An Analysis Batch is a sequence of samples, analyzed within a 24-hour period, of no more than 20 field samples and includes all required QC samples (LSMB, CCCs, the LFSM and LFSMD). The required QC samples are not included in counting the maximum field sample total of 20. LC-MS/MS conditions for the Analysis Batch must be the same as those used during calibration.

11.4.1 Analyze Initial CCC. After a valid calibration is established, begin every Analysis Batch by analyzing an initial low-level CCC. This initial CCC must be within 50–150% of the true value for each method analyte and must pass both the pre-analysis standard(s) area response criterion (Section 9.2.2.4) and the pre-extraction isotope recovery criterion (Section 9.2.2.6). The initial CCC confirms that the calibration is still valid. Failure to meet the QC criteria requires corrective action and may require recalibration prior to analyzing samples.

11.4.2 Analyze Field and QC Samples. After the initial CCC, continue the Analysis Batch by analyzing an LSMB, followed by the field samples and QC samples. Analyze a mid- or high-level CCC after every ten field samples and at the end of each Analysis Batch. Do not count QC samples (LSMBs, FDs, LFSMs, LFSMDs) when calculating the required frequency of CCCs.

11.4.3 Analyze Final CCC. The last injection of the Analysis Batch must be a mid- or high-level CCC. The acquisition start time of the final CCC must be within 24 hours of the acquisition start time of the low-level CCC at the beginning of the Analysis Batch. More than one Analysis Batch

within a 24-hour period is permitted. An Analysis Batch may contain field and QC samples from multiple extraction batches.

11.4.4 Initial Calibration Frequency. A full calibration curve is not required before starting a new Analysis Batch. A previous calibration can be confirmed by running an initial, low-level CCC followed by an LSMB. If a new calibration curve is analyzed, an Analysis Batch run immediately thereafter must begin with a low-level CCC and an LSMB.

12.0 Data Analysis and Calculations

12.1 Calculation Nomenclature.

A_s = Area of the characteristic mass for the compound in the continuing calibration verification sample.

A_{is} = Area of the characteristic mass of the pre-extraction isotopically labeled standard in the continuing calibration verification sample.

C_{is} = Concentration of the pre-extraction isotopically labeled standard (pg/µL).

C_s = Concentration of the native compound in the continuing calibration standard (pg/µL).

A_i = Integrated ion current for the isotopically labeled compound.

A_n = Integrated ion current for the target native compound.

C_i = Concentration of the labeled compound used to perform isotope recovery correction, pg/µL.

C_n = Concentration of the target native compound, pg/µL.

C_{ndscm} = Concentration of target native compound i in the emission gas, pg/dscm.

C_{next} = Concentration of target native compound i in the extract, pg.

D = Difference in the RRF of the continuing calibration verification compared to the average RRF of the initial calibration, percent (%).

dscm = Dry standard cubic meters of gas volume sample measured by the dry gas meter, corrected to standard conditions.

R* = Recovery of labeled compound standards, %.

RSD = Relative standard deviation, in this case, of RRFs over the five calibration levels, %.

SD_{RRF} = Standard deviation of initial calibration RRFs.

V_{ext} = Extract volume, μL.

12.2 Source gas volume calculations. Carry out calculations for stack gas velocity, volumetric flow rate, sampling volume, moisture, isokinetic variation following the procedures in Section 12 of Method 5 of appendix A-3 to 40 CFR part 60, with the following additions.

12.3 Qualitative Identification of Target Compounds.

12.3.1 Qualitative Identity of Peaks by Retention Times. At the conclusion of analysis data acquisition, use the same software settings established during the calibration procedure to qualitatively identify analyte peaks in the predetermined retention time windows. Confirm the identity of each analyte by comparing its retention time to that of the corresponding analyte peak in an initial calibration standard or CCC.

12.3.2 Qualitative Identity by Confirming the Precursor and Product Ions. Confirm that the native and pre-extraction isotope precursor and product ions are consistent with the continuing calibration results. The signals for all characteristic masses shall be present and shall maximize within the same two consecutive scans. The retention time difference between the native analyte

and its labeled analog shall agree within ±6 scans or ±6 seconds (whichever is greater) of this difference in the continuing calibration standard.

12.4 Recovery of Labeled Compound Standards. Use the following equation to determine the recovery of any labeled compounds, including pre-sampling spikes, pre-extraction filter spike, pre-extraction spikes, and pre-analysis spikes. Verify and report the percent recovery of the pre-extraction isotopic labeled spike. The recovery performance criteria and actions if performance criteria are not met for these spikes is in Section 9 of this method.

$$R^* = \frac{conc.\ found}{conc.\ spiked}\ x\ 100\% \qquad \text{Eq. 45-9}$$

12.5 Quantitative Determination of Target Compounds by Isotope Dilution. Isotope dilution in this method is performed by adding a known amount of a labeled compound to every sample prior to extraction. Correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon extraction, concentration, and chromatography.

Because quantitative isotopically labeled analogs are not available for all the PFAS target compounds in this procedure, quantitation of certain target PFAS is performed using closely eluting surrogates, resulting in added uncertainty for those PFAS targets. Procedures in this section must be followed to identify and report both the identity and quantity of PFAS found in source gas samples. When the concentration of target compounds exceeds the calibration range and sample dilution is required, pre-extraction isotope dilution standards may not be detectable and calculation of the quantity of target may revert to standard analytical approaches that use native response factors from the daily CCV.

12.5.1 PFOA Quantification. For PFOA, identify the branched and linear isomers by analyzing a technical-grade standard that includes both linear and branched isomers as directed and ensure that all isomers elute within the same acquisition segment. Quantitate field samples and fortified matrix samples by integrating the total response, accounting for peaks that are identified as linear and branched isomers. Quantitate based on the standard containing only the linear isomer.

12.5.2 PFHxS, PFOS, and Other Analytes with Technical-Grade Standards. Multiple chromatographic peaks, representing branched and linear isomers, have been observed for current standards of PFHxS and PFOS using the LC conditions in this method. For PFHxS and PFOS, all the chromatographic peaks observed in the standard 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 standard for analytes with quantitative standards containing the branched and linear isomers.

12.5.3 Target Compound Concentration Calculation. Calculate the concentration of each of the target compounds in each of the sample fractions using the multipoint calibration and the measured sample volume, including compensation for archived splits of the sample following the procedures in this section. Calculations must use all available digits of precision. Final reported concentrations may be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures. Results must be reported individually for the filter, primary sorbent, impinger(s), and backup sorbent fractions. Report all results as total mass per media fraction corrected for sample aliquot, sample dilution, and sample concentration as described in the following sections of this method.

12.5.3.1 Sample Concentrations Below the Lowest Calibration Standard. It is important to estimate the concentrations of target PFAS compounds below the lowest calibration standard concentration as well as below the QRL whenever possible. Samples may be concentrated and reanalyzed, or calibration curves may be extended to lower concentrations as necessary if initial concentration determination shows results below the lowest calibration standard. Concentrations may be estimated using the calibration equation or by other accepted approaches (e.g., using the RRF for the lowest calibration standard). The lowest calibration point may not be lower than three times the MDL.

12.5.3.1.1 Concentrations Between the QRL and MDL. Report concentrations between the detection limit (MDL) and the QRL for target compounds in each fraction with a J flag and explain the meaning of the J flag in your laboratory report, including the approach for estimating concentrations below the lowest calibration standard.

12.5.3.1.2 Concentrations Below the MDL. Report results below the detection limit (MDL) with a BDL flag and explain the meaning of the BDL flag in your laboratory report, including the approach for estimating concentrations below the lowest calibration standard.

12.5.4 Sample Concentrations Above the Highest Calibration Standard. Report concentrations of analytes that exceeded the calibration range in the original sample based on measurement in a diluted sample. Incorporate the dilution factor into final concentration calculations.

12.6 Quantitation Formulas.

12.6.1 Response Factors. Calculate daily response factors for each of the target analytes in the continuing calibration verification sample using the following equation:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Eq. 45-10}$$

Where,

A_{is} = Area of the characteristic mass of the pre-extraction isotopically labeled standard in the continuing calibration verification sample.

A_s = Area of the characteristic mass for the native compound in the continuing calibration verification sample.

C_{is} = Concentration of the pre-extraction isotopically labeled analog in the standard (pg/µL).

C_s = Concentration of the native compound in the continuing calibration standard (pg/µL).

Confirm that the daily response factors for each target analyte meet the QC criteria in Section 9 of this method.

12.6.2 Isotope Dilution Quantification of Target Compounds in Sample Extracts.

12.6.2.1 Proceed with target compound quantitation based on the type of isotopic labeled standard available that was used for each method analyte. If standards containing the branched and linear isomers cannot be purchased (i.e., only the linear isomer is available), only the linear isomer can be identified and quantitated in field samples and QC samples. Target analytes and branched isomers that do not have corresponding isotopic labels must be reported separately showing which native and isotopic labels were used to generate semiquantitative results for the analytes and isomers.

12.6.2.2 The response of each target compound (RR) relative to its labeled analog is determined using the area responses for each calibration standard, as follows:

$$RR = \frac{(A_n)(Ci)}{(A_i)(C_n)} \qquad \text{Eq. 45-11}$$

Where,

A_n = Areas of the characteristic m/z for the target compound(s).

A_i = Areas of the peak representing the primary m/z for the labeled compound.

C_i = Concentration of the labeled compound in the calibration standard.

C_n = Corresponding concentration of the native compound in the calibration standard.

12.6.2.3 Calculate the Concentration of Individual Target Compounds in the Extract by Isotope Dilution (pg/µL). This equation corrects for the target native compound recovery by its labeled pre-extraction spike analog. To accomplish this the pre-extraction spike, labeled compound concentrations must remain constant. Compute the concentration in the extract using the following equation:

$$C_{ex}\left(\frac{\rho g}{\mu L}\right) = \frac{(A_n)(C_i)}{(A_i)(RR)} \qquad \text{Eq. 45-12}$$

Where:

C_{ex} = Concentration of the target compound in the extract in pg/µL.

C_i = Concentration of the labeled compound in the calibration standard in pg/µL.

12.6.2.4 Total Mass of the Individual Target Compounds in the Sample Extract (pg). Calculate the mass for each target compound in each sample fraction using the concentration of the

compound in the extract and the volume of extract, including any dilution, aliquots and/or archiving.

$$M_{total} = \frac{(C_{ex})(V_{ext})}{f} \qquad \text{Eq. 45-13}$$

Where,

f = Fraction of the original sample extract before concentration taken for analysis (volume extracted/volume concentrated).

C_{ex} = Concentration of the compound in the extract in pg/µL.

Vext = Final extract volume after concentration and/or dilution in mL.

12.6.3 Concentration of the Individual Target Compound or in the Emission Gas (pg/dscm). Calculate the gaseous emission concentration for each target compound based on the sum of the measured mass for each sample train fraction in which PFAS were detected.

$$C_{dscm} = \frac{M_{sum\ total}}{dscm} \qquad \text{Eq. 45-14}$$

Where,

dscm = Standard dry cubic meters of gas collected in the sampling run.

12.6.3.1 Stack Detectable Limit (SDL). Calculate the gaseous emission, in-stack DL (pg/dscm) for each target compound based the sum of the sample-specific MDL masses for sample train fractions 1, 2 and 3, divided by the standard dry cubic meters of gas collected in the sampling run.

$$SDL = \frac{M_{MDLSum}}{dscm} \qquad \text{Eq. 45-15}$$

Where,

M_{MDLSum} = Sum of the sample-specific MDL masses for sample train fractions 1, 2 and 3.

12.7 Data Reporting. Report the following data in the emissions test reports.

12.7.1 Analytical Data. Include the following data and information in analytical data reports and emissions data test report.

12.7.1.1 Calibration Data. Include the number of calibration points and associated concentrations, including the lowest point in the calibration curve. Provide the calibration information used to derive the quantitative relationship and the approach used. Report the agreement between the calculated value and known value for each calibration point (See Section 10.4.5 for calibration criteria).

12.7.1.2 MDL Study Data. Report the results for the MDL study identified and described in Section 9.2.1.3.

12.7.1.2.1 MDL Concentration and Mass for Each Fraction. Report the study's individual MDLs established for Fractions 1 – 3. Include the overall mass for each analyte as well as the associated volumetric concentration (pg/µL) used for determining the MDL mass specific to a collected emissions sample.

12.7.1.2.2 MDL Accuracy Data. Report the accuracy data from the MDL study and Section 9.2.1.6.

12.7.1.2.3 MDL Precision Data. Report the precision data from the MDL study and Section 9.2.1.5.

12.7.1.3 Laboratory Fortified Media Blank Samples Data. Report the results of the dual level LFMB samples from Section 9.2.2.4.

12.7.1.4 Laboratory Blanks. Report the target PFAS compound masses for all laboratory blanks.

12.7.1.5 Sample Train Analytical Data. Report all field sample analytical data, including blanks.

12.7.1.5.1 Sample-Specific Concentration and Mass for Each Fraction. Report the sample-specific analytical mass/volume (liquid) concentration and associated mass for each PFAS target compound and each fraction, inclusive of sample-specific final extract volumes, archive volumes, dilutions, etc.

12.7.1.4.2 Sample-Specific MDL Mass for Each Fraction. Report the sample-specific analytical MDL mass/volume (liquid) concentration and associated mass for each PFAS target compound and each fraction, inclusive of total sample-specific final extract volumes, archive volumes, dilutions, etc.

12.7.1.4.3 Sample-Specific QRL Mass for Each Fraction. Report the sample-specific analytical QRL mass/volume (liquid) concentration and associated mass for each PFAS target compound and each fraction, inclusive of total sample-specific final extract volumes, archive volumes, dilutions, etc.

12.7.1.4.4 Pre-extraction Standard Recoveries for Each Fraction. Report the pre-extraction standard recoveries for each standard, for each fraction.

12.7.1.4.5 Pre-Sampling Standard Mass and Recoveries. Report PSS mass for Fractions 2 (primary XAD-2 adsorbent and rinses) and 3 (condensate/impingers and rinse) and individual and combined recoveries.

Note: The pre-sampling standard recoveries include both Fractions 2 and 3 and the pre-sampling standard may have migrated from the XAD-2 to the impingers.

12.7.2 Sampling and Emissions Data. Include the following data and information in the emissions data test report.

12.7.2.1 Emissions Data. For each run, report the target compound masses measured for each fraction. Flag reported masses to indicate if they are in the quantitative range, estimated, or non-detect. Report the associated gaseous concentration for that run, based on the sum of detected fractions and the gaseous sample volume collected for that run.

12.7.2.2 Stack Detection Limits (SDLs). For each run, report the sample-specific SDLs based on run-specific QRL and MDL masses (sum of fractions 1-3) and the gaseous sample volume collected for that run.

12.7.2.3 Flag final sum of fractions 1 – 3 results as described in Section 9.5.

13.0 Method Performance

Data to support OTM-45 Method Performance to date is limited. This method has been developed based on a combination of empirical knowledge and data as well as incorporation of procedures and concepts adapted from other methods and measurement practices. EPA/ORD research, including field evaluation testing, has resulted in data that support the specified OTM-

45 method performance criteria, including pre-extraction standard and pre-sampling standard isotopic label recovery criteria. Moreover, these performance criteria are further confirmed by communications with, and data shared by commercial analytical laboratories. Tables 45-10 and 45-11 present the pre-sampling standard recoveries and pre-extraction standard recoveries achieved, respectively, as part of an ORD OTM-45 field evaluation. In general, pre-extraction standard recoveries for Fractions 1 (Filter) and 3 (Impingers) were greater than for Fraction 2 (XAD-2). An average pre-sampling standard recovery of 100.3% was observed for PFOA, while an average pre-sampling standard recovery of 73.0% was observed for PFOS. Additional pre-sampling standard candidate compounds may be used to better represent overall measurement performance. The pre-extraction standard recoveries presented in Table 45-10 also support OTM-45 performance criteria.

Table 45-12 presents the calculated in-stack detection levels, based on both QRLs and MDLs and a nominal 3 m^3 sample volume. The values represent the sum of Fractions 1, 2, and 3. The in-stack detection levels reported indicate that measurements in the pg/m^3 range are possible for the majority of OTM-45 targeted PFAS compounds.

The preparation and release of this method is intended to further establish data to support refinement of these initial performance criteria.

The collection of blanks, in replicate and representing multiple forms, is particularly important for data interpretation and validation. Managing PFAS contamination from a variety of sources, particularly XAD-2, has been a critical and acknowledged factor to collecting emissions data of known and acceptable quality. The recent application of PFAS emissions testing has resulted in advancements to minimizing PFAS contamination. However, the comprehensive collection of

laboratory and field sampling blank samples remains critical to identifying sources of contamination and an inherent component to interpreting results from this method.

14.0 Pollution Prevention

The target compounds used as standards in this method are prepared in extremely small amounts and pose little threat to the environment when managed properly. Prepare standards in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

15.0 Waste Management

15.1 The laboratory is responsible for complying with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. The laboratory must also comply with any sewage discharge permits and regulations. The EPA's *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001) provides an overview of requirements.

15.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *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.

16.0 Bibliography

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3) EPA Method 1633
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11) Field Sampling Materials Unlikely Source of Contamination for Perfluoroalkyl and Polyfluoroalkyl Substances in Field Samples.
Alix E. Rodowa, Emerson Christie, Jane Sedlak, Graham F. Peaslee, Dorin Bogdan, Bill DiGuiseppi, and Jennifer A. Field*, Environ. Sci. Technol. Lett. 2020, 7, 3, 156–163, https://pubs.acs.org/doi/10.1021/acs.estlett.0c00036

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 45-1. Targeted PFAS Analytes

Common Name[a]	*Abbreviated Name*	*CAS*[b] *Registry Number*	*Pre-Sampling Standards*	*Pre-Extraction Standard/ Quantification Reference Compounds*	*Pre-Analysis Standards*
Perfluoroalkylcarboxylic acids (PFCAs)					
Perfluorobutanoic acid[1,3,4,5]	PFBA	375-22-4	$^{13}C_3$-PFBA	$^{13}C_4$-PFBA	
Perfluoropentanoic acid[1,3,4,5]	PFPeA	2706-90-3		$^{13}C_5$-PFPeA	$^{13}C_3$-PFPeA
Perfluorohexanoic acid[1,2,3,4,5]	PFHxA	307-24-4		$^{13}C_5$-PFHxA	
Perfluoroheptanoic acid[1,2,3,4,5]	PFHpA	375-85-9		$^{13}C_4$-PFHpA	
Perfluorooctanoic acid[1,2,3,4,5]	PFOA	335-67-1	$^{13}C_4$-PFOA	$^{13}C_8$-PFOA	$^{13}C_2$-PFOA
Perfluorononanoic acid[1,2,3,4,5]	PFNA	375-95-1		$^{13}C_9$-PFNA	
Perfluorodecanoic acid[1,2,3,4,5]	PFDA	335-76-2		$^{13}C_6$-PFDA	$^{13}C_2$-PFDA
Perfluoroundecanoic acid[1,2,3,4,5]	PFUnDA	2058-94-8		$^{13}C_7$-PFUnA	
Perfluorododecanoic acid[1,2,3,4,5]	PFDoA	307-55-1	$^{13}C_{12}$-PFDoA	$^{13}C_2$-PFDoA	
Perfluorotridecanoic acid[2,3,4,5]	PFTrDA	72629-94-8		$^{13}C_2$-PFTeDA	
Perfluorotetradecanoic acid[2,3,4,5]	PFTeDA	376-06-7		$^{13}C_2$-PFTeDA	
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5		$^{13}C_2$-PFHxDA	
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6		$^{13}C_2$-PFHxDA	
Perfluorinated sulfonic acids (PFSAs)					
Perfluoro-1-butanesulfonic acid[1,2,3,4,5]	PFBS	375-73-5	$^{13}C_4$-PFBS	$^{13}C_3$-PFBS	
Perfluoro-1-pentanesulfonic acid[1,3,5]	PFPeS	2706-91-4		$^{13}C_3$-PFHxS	
Perfluoro-1 -hexanesulfonic acid[1,2,3,4,5]	PFHxS	355-46-4		$^{13}C_3$-PFHxS	$^{13}C_6$-PFHxS
Perfluoro-1-heptanesulfonic acid[1,3,5]	PFHpS	375-92-8		$^{13}C_8$-PFOS	
Perfluoro-1-octanesulfonic acid[1,2,3,4,5]	PFOS	1763-23-1	$^{13}C_4$-PFOS	$^{13}C_8$-PFOS	
Perfluoro-1-nonanesulfonic acid[3,5]	PFNS	68259-12-1		$^{13}C_8$-PFOS	
Perfluoro-1-decanesulfonic acid[3,5]	PFDS	335-77-3		$^{13}C_8$-PFOS	
Perfluorododecanesulfonic acid[5]	PFDoS	79780-39-5		$^{13}C_8$-PFOS	
Perfluorinated sulfonamides (FOSAs)					
Perfluoro-1-octanesulfonamide[3,5]	FOSA	754-91-6		$^{13}C_8$-FOSA	
N-Methylperfluorooctanesulfonamide [5]	MeFOSA	31506-32-8		d_3-MeFOSA	
N-ethylperfluorooctanesulfonamide [5]	EtFOSA	4151-50-2		d_5-EtFOSA	
Perfluorinated sulfonamide ethanols (FOSEs)					
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol [5]	N-MeFOSE	24448-09-7		d_7-N-MeFOSE	
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol [5]	N-EtFOSE	1691-99-2		d_9-N-EtFOSE	
Perfluorinated sulfonamidoacetic acids (FOSAAs)					
N-methyl perfluorooctanesulfonamido-acetic acid[2,3,5]	MeFOSAA	2355-31-9		d_3-N-MeFOSAA	
N-ethyl perfluorooctanesulfonamido-acetic acid[2,3,5]	EtFOSAA	2991-50-6		d_5-N-EtFOSAA	
Fluorotelomer sulfonates (FTSs)					

Common Name[a]	*Abbreviated Name*	*CAS*[b] *Registry Number*	*Pre-Sampling Standards*	*Pre-Extraction Standard/ Quantification Reference Compounds*	*Pre-Analysis Standards*
1H,1H,2H,2H-Perfluorohexane sulfonic acid[1,3,5]	4:2 FTS	757124-72-4		$^{13}C_2$-4:2FTS	
1H,1H,2H,2H -Perfluorooctane sulfonic acid[1,3,5]	6:2 FTS	27619-97-2		$^{13}C_2$-6:2FTS	
1H,1H,2H,2H -Perfluorodecane sulfonic acid[1,3,5]	8:2 FTS	39108-34-4		$^{13}C_2$-8:2FTS	
1H,1H,2H,2H-perfluorododecane sulfonate	10:2 FTS	120226-60-0		$^{13}C_2$,d_4-10:2FTS	
Fluorinated Replacement Chemicals					
4,8-Dioxa-3H-perfluorononanoic acid[1,2,5]	ADONA	919005-14-4		$^{13}C_6$-PFDA	
Hexafluoropropylene oxide dimer acid[1,2,5]	HFPO-DA (GenX)	13252-13-6		$^{13}C_3$-HFPO-DA	
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid[1,2,5]	9Cl-PF3ONS (F-53B Major)	756426-58-1		$^{13}C_8$-PFOS	
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid[1,2,5]	11Cl-PF3OUdS (F-53B Minor)	763051-92-9		$^{13}C_8$-PFOS	
Additional Targets					
Nonafluoro-3,6-dioxaheptanoic acid[1,5]	NFDHA	151772-58-6		$^{13}C_5$-PFHxA	
Perfluoro(2-ethoxyethane)sulfonic acid[1,5]	PFEESA	113507-82-7		$^{13}C_3$-PFBS	
Perfluoro-4-methoxybutanoic acid[1,5]	PFMBA	863090-89-5		$^{13}C_5$-PFPeA	
Perfluoro-3-methoxypropanoic acid[1,5]	PFMPA	377-73-1		$^{13}C_5$-PFPeA	
Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate)[4]	PFecHS	67584-42-3		$^{13}C_3$-PFHxS	
2H-perfluoro-2-octenoic acid[4]	6:2 FTUCA (FHUEA)	70887-88-6		$^{13}C_2$-FHUEA	
2H-perfluoro-2-decenoic acid[4]	8:2 FTUCA (FOUEA)	70887-84-2		$^{13}C_2$-FOUEA	
2-perfluorohexyl ethanoic acid[4]	6:2 FTCA (FHEA)	53826-12-3		$^{13}C_2$-FHEA	
2-perfluorooctyl ethanoic acid[4]	8:2 FTCA (FOEA)	27854-31-5		$^{13}C_2$-FOEA	
2-perfluorodecyl ethanoic acid[4]	10:2 FTCA (FDEA)	53826-13-4		$^{13}C_2$-FDEA	
3:3 Fluorotelomer carboxylic acid [5]	3:3 FTCA	356-02-5		$^{13}C_5$-PFPeA	
5:3 Fluorotelomer carboxylic acid [5]	5:3 FTCA	914637-49-3		$^{13}C_4$-PFHpA	
7:3 Fluorotelomer carboxylic acid [4, 5]	7:3 FTCA	812-70-4		$^{13}C_9$-PFNA	

[a] Some PFAS are commercially available as ammonium, sodium, and potassium salts. This method measures all forms of the analytes as anions while the identity of the counterion is inconsequential. Analytes may be purchased as acids or as any of the corresponding salts (see additional information in Section 7.3.9).

[b] Chemical Abstract Service.

[1] Compound targeted in EPA Method 533

[2] Compound targeted in EPA Method 537.1

[3] Compound targeted in EPA Method 8327

[4] Compound targeted in ASTM Method D7968

[5] Compound targeted in EPA Method 1633

Table 45-2 MS/MS Conditions and Characteristic Ions

Analyte	*Precursor Ion (m/z)*	*Primary Product Ion (m/z)*	*Secondary Product Ion (m/z)*
PFBA	213	169	---
$^{13}C_3$-PFBA	216	172	---
$^{13}C_4$-PFBA	217	172	---
PFPeA	263	219	69
$^{13}C_3$-PFPeA	266	222	---
$^{13}C_5$-PFPeA	268	223	---
PFHxA	313	269	119
$^{13}C_5$-PFHxA	318	273	---
PFHpA	363	319	169
$^{13}C_4$-PFHpA	367	322	---
PFOA	413	369	169
$^{13}C_2$-PFOA	415	370	---
$^{13}C_4$-PFOA	417	372	---
$^{13}C_8$-PFOA	421	376	---
PFNA	463	419	169
$^{13}C_9$-PFNA	472	427	---
PFDA	513	469	169
$^{13}C_2$-PFDA	515	470	---
$^{13}C_6$-PFDA	519	474	---
PFUnA	563	519	169
$^{13}C_7$-PFUnA	570	525	---
PFDoA	613	569	169
$^{13}C_2$-PFDoA	615	570	---
$^{13}C_{12}$-PFDoA	625	580	---
PFTrDA	663	619	169
PFTeDA	713	669	169
$^{13}C_2$-PFTeDA	715	670	---
PFHxDA	813	769	169
$^{13}C_2$-PFHxDA	815	770	---
PFODA	913	869	169
PFBS	299	80	99
$^{13}C_3$-PFBS	302	80	---
$^{13}C_4$-PFBS	303	80	---
PFPeS	349	80	99
PFHxS	399	80	99
$^{13}C_3$-PFHxS	402	80	---
$^{13}C_6$-PFHxS	405	80	---
PFHpS	449	80	99
PFOS	499	80	99
$^{13}C_4$-PFOS	503	80	---
$^{13}C_8$-PFOS	507	80	---

Analyte	*Precursor Ion (m/z)*	*Primary Product Ion (m/z)*	*Secondary Product Ion (m/z)*
PFNS	549	80	99
PFDS	599	80	99
PFDoS	699	80	99
FOSA	498	78	169
$^{13}C_8$-FOSA	506	78	---
MeFOSA	512	219	169
d_3-MeFOSA	515	219	---
EtFOSA	526	219	169
d_5-EtFOSA	531	219	---
N-MeFOSE	616	59	---
d_7-N-MeFOSE	623	59	---
N-EtFOSE	630	59	---
d_5-N-EtFOSE	635	59	---
d_9-N-EtFOSE	639	59	---
MeFOSAA	570	419	483
d_3-N-MeFOSAA	573	419	---
EtFOSAA	584	419	526
d_5-N-EtFOSAA	589	419	---
4:2FTS	327	307	81
$^{13}C_2$-4:2FTS	329	309	---
6:2FTS	427	407	81
$^{13}C_2$-6:2FTS	429	409	---
8:2FTS	527	507	81
$^{13}C_2$-8:2FTS	529	509	---
10:2FTS	627	607	81
$^{13}C_2$,d_4-10:2FTS	633	612	---
ADONA	377	251	85
HFPO-DA	285	169	185
$^{13}C_3$-HFPO-DA	287	169	---
9Cl-PF3ONS	531	351	83
11Cl-PF3OUdS	631	451	83
NFDHA	295	201	85
PFEESA	315	135	69
PFMBA	279	85	235
PFMPA	229	85	185
PFecHS	461	381	99
8:2 FTUCA	457	393	343
$^{13}C_2$-FOUEA	459	394	344
10:2 FTCA	577	493	63
$^{13}C_2$-FDEA	579	494	64
8:2 FTCA	477	393	63
$^{13}C_2$-FOEA	479	394	64
6:2 FTUCA	357	293	243

Analyte	*Precursor Ion (m/z)*	*Primary Product Ion (m/z)*	*Secondary Product Ion (m/z)*
$^{13}C_2$-FHUEA	359	294	244
6:2 FTCA	377	293	63
$^{13}C_2$-FHEA	379	294	64
3:3 FTCA	241	177	117
5:3 FTCA	341	237	217
7:3 FTCA	441	337	317

Table 45-3 Fortification and Recovery Solutions for Per- and Polyfluoroalkyl Substances[a]

Compound	Amount (ng)[b]	Spike Recovery (percent)
Pre-sampling Standards		
$^{13}C_3$-PFBA	125	70-130
$^{13}C_4$-PFOA	125	70-130
$^{13}C_{12}$-PFDoA	125	70-130
$^{13}C_4$-PFBS	125	70-130
$^{13}C_4$-PFOS	125	70-130
Pre-extraction Standards		
$^{13}C_4$-PFBA	100	20-200
$^{13}C_5$-PFPeA	100	20-200
$^{13}C_5$-PFHxA	100	20-200
$^{13}C_4$-PFHpA	100	20-200
$^{13}C_8$-PFOA	100	20-200
$^{13}C_9$-PFNA	100	20-200
$^{13}C_6$-PFDA	100	20-200
$^{13}C_7$-PFUnA	100	20-200
$^{13}C_2$-PFDoA	100	20-200
$^{13}C_2$-PFTeDA	100	20-200
$^{13}C_2$-PFHxDA	100	20-200
$^{13}C_3$-PFBS	100	20-200
$^{13}C_3$-PFHxS	100	20-200
$^{13}C_8$-PFOS	100	20-200
$^{13}C_8$-FOSA	100	20-200
d_3-MeFOSA	100	20-200
d_5-EtFOSA	100	20-200
d_7-N-MeFOSE	100	20-200
d_9-N-EtFOSE	100	20-200
d_3-N-MeFOSAA	100	20-200
d_5-N-EtFOSAA	100	20-200
$^{13}C_2$-4:2FTS	100	20-200
$^{13}C_2$-6:2FTS	100	20-200
$^{13}C_2$-8:2FTS	100	20-200
$^{13}C_2$,d_4-10:2FTS	100	20-200
$^{13}C_3$-HFPO-DA	100	20-200
$^{13}C_2$-FOUEA	100	20-200

Compound	Amount (ng)[b]	Spike Recovery (percent)
$^{13}C_2$-FDEA	100	20-200
$^{13}C_2$-FOEA	100	20-200
$^{13}C_2$-FHUEA	100	20-200
$^{13}C_2$-FHEA	100	20-200
Pre-analysis Standards		
$^{13}C_3$-PFPeA	25	S/N≥10
$^{13}C_2$-PFOA	25	S/N≥10
$^{13}C_2$-PFDA	25	S/N≥10
$^{13}C_6$-PFHxS	25	S/N≥10

[a] Changes in the amounts of spike standards added to the sample or its representative extract will necessitate an adjustment of the calibration solutions to prevent the introduction of inconsistencies.
[b] Spike amounts assume three quarters of the extract will be archived before cleanup. Spike amounts may be adjusted for different split levels. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used.

Table 45- 4 Sample Storage Conditions[a] and Laboratory Hold Times

Stage	Type	Storage Conditions	Laboratory Holding time
Field Collection	All Field Samples	Store on ice or refrigerated ≤6 °C (43°F)	N/A
Shipping/Transport	All Field Samples	Ship on ice ≤6 °C (43°F) Follow procedures in ASTM D6911-15	N/A
Laboratory Storage: Before Extraction	All Sampling Train Rinses	Store refrigerated ≤6 °C (43°F)	Extract within 30 days of collection
	Particulate Filter Samples		
	Adsorbent Samples (XAD-2)		
Laboratory Storage: After Extraction (archived)	All Archived Extracted Samples	Store refrigerated ≤6 °C (43°F)	Analyze within 30 days of extraction

[a] All samples must be stored in the dark after collection.

Table 45-5. General QA/QC Requirements for OTM-45

Section	Requirement	Specification and Frequency	Acceptance Criteria	Consequences and Corrective Actions
Sampling Quality Controls (Section 9.1)				
9.1.2	Field Sampling Media Blank (FSMB)	Represents the sampling media and reagents associated with field sample collection. One per each test series.	Levels should be ≤ compound MDL.	Analysis of the FSMBs should be compared to the background level criteria in Section 9.2.2.1. Failure to meet these levels does not invalidate the sampling run. If > MDL, flag data. The measured target compound mass in each fraction will need to be reported and used to interpret sample assess impact on results. .
9.1.3	Sample Train Proof Blank (STPB)	At least one STPB per each test series.	Levels ≤10% of actual samples.	If >10%, flag data and assess impact on results.
9.1.4	Sample Train Field Blank (STFB)	Optional: At least one STPB per each test series when glassware is being reused..	Levels ≤10% of actual samples	If >10%, flag data and assess impact on results.
9.1.5	Pre-Sampling Standards	Added to each XAD-2 adsorbent cartridge prior to sampling. Indicates sample collection and recovery efficiency.	≥70% and ≤130% recovery of all spike standards as the sum of the recovery of sampling train fractions 2 and 3.	Recoveries below the acceptable range of 70-130% for the pre-sampling standard spikes may require a root cause evaluation. If the recovery of all the pre-sampling standard adsorbent spikes is below 70%, but, greater than 50%, the results have not met the recoveries experienced during method development but may still be acceptable. Flag recoveries that are between 50 and 70% and describe their potential impact on results. If the pre-sampling standard recoveries are less than 50%, the data for that train are not considered valid.

9.1.6	Secondary XAD-2	Determines the relative breakthrough (BT) of each target through the OTM-45 train.	≤10% BT for each target compound. .	For any BT ≥ 10%, add the fraction 4 mass to the total sample mass for emissions calculations and flag data. If fractions 1-3 are below QRL, do not add to the total sample mass.
Ongoing Quality Control Requirements (Section 9.2.2)				
9.2.2.1.1	Sampling Media Background Level Checks	Confirm sample media background before use for sampling.	Levels should be ≤ compound MDL.	If >MDL, further clean sampling media until levels are ≤ MDL.
9.2.2.1.2	Laboratory Sample Media Blank (LSMB)	Analyze a LSMB for each sampling medium and reagent with each extraction batch **and** ≥1 LSMB when method analytes exceed the calibration range.	Levels should be ≤ compound MDL.	If >MDL, flag data and assess impact on results Resolve source of contamination before proceeding to additional analyses.
9.2.2.3	Calibration Acceptance Criteria	Evaluate the initial concentration of each analyte as an unknown against its regression equation (Section 10.4).	Between 90-110% of each analyte true value.	Reanalyze the calibration standards, restrict the range of calibration, or perform instrument maintenance. If failure is due to contamination or standard degradation, prepare fresh calibration standards and repeat initial calibration.
9.2.2.3.1	Continuing Calibration Check (CCC)	Analyze CCC at the beginning of each analysis batch, after every tenth field sample, and at the end of the analysis batch.	Beginning CCC must be equal to QRL for each analyte. Must be within 70-130% of true value.	If the CCC fails because concentration is >130% (150% for low-level CCC) and field sample extracts show no concentrations above the MDL for that analyte, non-detects can be reported without re-analysis. See Section 10.6 for Corrective Action.
9.2.2.4	Laboratory Fortified Media Blanks (LFMB)	Duplicate low and high LFMBs are required with each extraction batch for each fraction.	Analytes fortified near or at the lowest calibration point must be within 50-150% of the true value. Analytes fortified at all other concentrations must be within 70–130% of the true value.	If the LFMB results do not meet these criteria, the laboratory must investigate the cause for this failure, report their findings and corrective action. Then report all data for the problem analytes with a note that LFMB accuracy criteria were not met.

9.2.2.5	Pre-Analysis Standard(s) Areas	The analyst must monitor the peak areas of the pre-analysis standards in all injections of the analysis batch.	The pre-analysis standards (as indicated by peak area) in any chromatographic run must be within 50-150% of the average area measured during the initial calibration.	If criteria are not met, reanalyze the extract in a subsequent analysis batch. If the pre-analysis standard(s) area fails to meet the acceptance criteria in the repeat analysis, or if multiple samples in a batch fail to meet the pre-analysis spike criteria, perform corrective action, and reanalyze the failed sample extracts.
9.2.2.6	Pre-Extraction Isotope Dilution	For each sample fraction, calculate the concentration and percent recovery of each isotope dilution analogue in field and QC samples using the average area in the initial calibration and internal standard.	Percent recovery must be within a range of 20-130%.	Recoveries below the acceptable range for pre-extraction spikes are an indication that sample preparation procedures did not adequately address sample and/or sample matrix processing to recover native target compounds. Compounds that fail this criterion must be flagged and reported as not quantitative because of QC failure. If this failure involves target compounds that are critical to the test objectives, this is a failure that requires root cause investigation and may require a repeat field sampling effort.
9.2.2.7	Calibration Verification using Quality Control Standards (QCS)	Perform a calibration verification during the IDC and at least quarterly after.	Results must be within 70-130% of the true value.	If accuracy fails, prepare fresh standard dilutions and repeat the calibration verification.
9.3	Method Modification QC Requirements	Perform after modifying chromatographic and MS/MS conditions.	Must pass IDC criteria. Must evaluate and document method performance in an archived field sample.	Repeat until IDC is passed.

Table 45-6 Initial Demonstration of Capability QC Requirements

Section	Requirement	Specification and Frequency	Acceptance Criteria
10.3.2	Establish Retention Times for Branched Isomers	Each time chromatographic conditions change.	All isomers of each analyte must elute within the same MRM window.
9.2.1.2	Demonstration of Low System Background	Analyze a LSMB after the highest standard in the calibration range. If an automated extraction system is used, an LSMB must be extracted on each port.	Confirm that the LSMB is free from contamination as defined in section 9.2.2.1.
9.2.1.3	Determination of MDL	7 LSMB and LFMB that are spiked within 2 to 10 times of the expected MDL. See 40 CFR Part 136 Appendix B.	Establishes detectable concentrations for each sampling train fraction. Sample Specific MDLs are reported inclusive of sample-specific dilutions, final volumes, aliquots, etc.
9.2.1.4	MDL Confirmation	Prepare a LSMB for each sampling media by spiking each media with native targets at the MDL and pre-extraction isotopic labeled standards at the concentration used to analyze field samples. Prepare and analyze the spiked LSMB. Fortify and analyze 7 replicate LFMBs at the proposed MDL concentration. Confirm that the Upper Prediction Interval of Results (PIR) and Lower PIR meet the recovery criteria.	Upper PIR ≤150% Lower PIR ≥50% If not met, the lowest calibration point has been set too low and must be confirmed again at a higher concentration.
9.2.1.5	Demonstration of Precision	Extract and analyze 7 replicate LFMBs near the mid-range concentration.	Percent relative standard deviation must be ≤20%.
9.2.1.6	Demonstration of Accuracy	Calculate mean recovery for replicates used in Section 9.2.1.5.	Mean recovery within 70–130% of the true value.
9.2.1.7	Lowest Calibration Concentration Confirmation	Establish a target concentration for the lowest calibration based on the intended use of the method. See subsections 9.1.2.7.1 - 9.2.1.7.2 for details.	Upper PIR ≤150% Lower PIR ≥50% If not met, the lowest calibration point has been set too low and must be confirmed again at a higher concentration.
9.2.1.8	Calibration Verification	Analyze mid-level QCS.	Results must be within 70–130% of the true value.

Note: All aspects of the IDC must be successfully performed prior to analyzing field samples. If any of the above fail, you must repeat until successful.

Table 45-7 Example HPLC Method Conditions

Time (min)	% 20 mM Ammonium acetate	% Methanol
Initial	95.0	5.0
0.5	95.0	5.0
3.0	60.0	40.0
16.0	20.0	80.0
18.0	20.0	80.0
20.0	5.0	95.0
22.0	5.0	95.0
25.0	95.0	5.0
35.0	95.0	5.0

Table 45-8 Recommended Initial Calibration (ICAL) (pg/µL)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Perfluoroalkylcarboxylic acids (PFCAs)							
PFBA	0.25	0.50	1	2.5	5	20	100
PFPeA	0.25	0.50	1	2.5	5	20	100
PFHxA	0.25	0.50	1	2.5	5	20	100
PFHpA	0.25	0.50	1	2.5	5	20	100
PFOA	0.25	0.50	1	2.5	5	20	100
PFNA	0.25	0.50	1	2.5	5	20	100
PFDA	0.25	0.50	1	2.5	5	20	100
PFUnDA	0.25	0.50	1	2.5	5	20	100
PFDoA	0.25	0.50	1	2.5	5	20	100
PFTrDA	0.25	0.50	1	2.5	5	20	100
PFTeDA	0.25	0.50	1	2.5	5	20	100
PFHxDA	0.25	0.50	1	2.5	5	20	100
PFODA	0.25	0.50	1	2.5	5	20	100
Perfluorinated sulfonic acids (PFSAs)							
PFBS	0.25	0.50	1	2.5	5	20	100
PFPeS	0.25	0.50	1	2.5	5	20	100
PFHxS	0.25	0.50	1	2.5	5	20	100
PFHpA	0.25	0.50	1	2.5	5	20	100
PFOS	0.25	0.50	1	2.5	5	20	100
PFNS	0.25	0.50	1	2.5	5	20	100
PFDS	0.25	0.50	1	2.5	5	20	100
PFDoS	0.25	0.50	1	2.5	5	20	100
Perfluorinated sulfonamides (FOSAs)							
FOSA	0.25	0.50	1	2.5	5	20	100
EtFOSA	0.25	0.50	1	2.5	5	20	100
MeFOSA	0.25	0.50	1	2.5	5	20	100
Perfluorinated sulfonamide ethanols (FOSEs)							
MeFOSE	0.25	0.50	1	2.5	5	20	100
EtFOSE	0.25	0.50	1	2.5	5	20	100
Perfluorinated sulfonamidoacetic acids (FOSAAs)							
EtFOSAA	0.25	0.50	1	2.5	5	20	100
MeFOSAA	0.25	0.50	1	2.5	5	20	100
Fluorotelomer sulfonates (FTS)							
4:2 FTS	0.25	0.50	1	2.5	5	20	100
6:2 FTS	0.25	0.50	1	2.5	5	20	100
8:2 FTS	0.25	0.50	1	2.5	5	20	100
10:2 FTS	0.25	0.50	1	2.5	5	20	100
Fluorinated Replacement Chemicals							
ADONA	0.25	0.50	1	2.5	5	20	100
HFPO-DA (GenX)	0.25	0.50	1	2.5	5	20	100
^{9}Cl-PF_3ONS (F-53B Major)	0.25	0.50	1	2.5	5	20	100
^{11}Cl-PF_3OUdS (F-53B Minor)	0.25	0.50	1	2.5	5	20	100
Additional Targets							
NFDHA	0.25	0.50	1	2.5	5	20	100
PFEESA	0.25	0.50	1	2.5	5	20	100
PFMBA	0.25	0.50	1	2.5	5	20	100
PFMPA	0.25	0.50	1	2.5	5	20	100
PFecHS	0.25	0.50	1	2.5	5	20	100
8:2 FTUCA (FOUEA)	0.25	0.50	1	2.5	5	20	100
10:2 FTCA (FDEA)	0.25	0.50	1	2.5	5	20	100

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
8:2 FTCA (FOEA)	0.25	0.50	1	2.5	5	20	100
6:2 FTUCA (FHUEA)	0.25	0.50	1	2.5	5	20	100
6:2FTCA (FHEA)	0.25	0.50	1	2.5	5	20	100
3:3 FTCA	0.25	0.50	1	2.5	5	20	100
5:3 FTCA	0.25	0.50	1	2.5	5	20	100
7:3 FTCA (FHpPA)	0.25	0.50	1	2.5	5	20	100

Table 45-9 Isotopic Dilution Pairs Initial Calibration (ICAL) Concentration (pg/µL)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Perfluoroalkylcarboxylic acids (PFCAs)							
$^{13}C_4$-PFBA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_5$-PFPeA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_5$-PFHxA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_4$-PFHpA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_8$-PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_9$-PFNA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_6$-PFDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_7$-PFUnA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-PFDoA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-PFTeDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-PFHxDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Perfluorinated sulfonic acids (PFSAs)							
$^{13}C_3$-PFBS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_3$-PFHxS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_8$-PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Perfluorinated sulfonamides (FOSAs)							
$^{13}C_8$-FOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d_3-MeFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d_5-EtFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Perfluorinated sulfonamide ethanols (FOSEs)							
d_7-N-MeFOSE	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d_9-N-EtFOSE	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Perfluorinated sulfonamidoacetic acids (FOSAAs)							
d_3-N-MeFOSAA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d_5-N-EtFOSAA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Fluorotelomer sulfonates (FTS)							
$^{13}C_2$-4:2FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-6:2FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-8:2FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-d_4-10:2FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Fluorinated Replacement Chemicals							
$^{13}C_3$-HFPO-DA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FOUEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FDEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FOEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FHUEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FHEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Pre-analysis Spiking Standard							
$^{13}C_3$-PFPeA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-PFDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_6$-PFHxS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Additional Targets							
$^{13}C_2$-FOUEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FDEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FOEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FHUEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
$^{13}C_2$-FHEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 45-10 Pre-Sampling Standard Recoveries

	Percent (%) Recovery			
Pre-Sampling Standard	Avg	RSD	Max	Min
13C8 PFOA	100.3	9.2%	111.0	89.0
13C8 PFOS	73.0	18.6%	85.0	58.0

Table 45-11 Pre-Extraction Standard Recoveries

	Fraction 1 (Filter) Percent (%) Recovery				**Fraction 2 (XAD-2)** Percent (%) Recovery				**Fraction 3 (Impingers)** Percent (%) Recovery			
Pre-Extraction Standard	Avg	%RSD	Max	Min	Avg	%RSD	Max	Min	Avg	%RSD	Max	Min
13C2 PFDA	115	10.7	128	96	101	8.7	116	87	92	6.6	103	81
13C2 PFDoA	104	9.7	120	91	59	21.2	98	32	77	15.2	98	58
13C2 PFHxA	99	7.9	109	84	104	7.3	114	88	87	4.7	94	78
13C2 PFTeDA	110	10.6	124	95	59	23.2	97	31	76	12.6	100	56
13C2 PFUnA	112	10.9	130	98	83	13.5	104	58	88	10.3	102	68
13C3 HFPO-DA	100	4.7	106	92	102	7.2	116	90	83	5.4	93	72
13C4 PFBA	89	6.6	102	80	75	12.8	90	44	84	5.7	92	74
13C4 PFHpA	104	10.6	117	83	107	8.1	118	93	90	5.8	100	82
13C4 PFOA	111	8.2	123	97	120	11.3	133	99	96	3.0	101	91
13C4 PFOS	114	10.4	128	93	103	14.7	130	81	99	5.1	107	91
13C5 PFNA	116	9.9	130	100	113	8.1	125	103	96	4.5	102	90
13C5 PFPeA	95	7.1	106	82	99	6.4	106	87	91	4.4	97	83
13C8 FOSA	107	9.6	120	91	94	11.9	112	75	83	13.0	105	68
18O2 PFHxS	112	8.9	122	99	112	6.3	125	105	96	5.4	105	88
d3-NMeFOSAA	120	7.6	131	106	101	9.0	117	85	78	19.0	108	54
d5-NEtFOSAA	135	9.4	145	118	94	14.7	114	75	79	19.4	110	57
M2-4:2 FTS	126	16.4	146	96	121	16.5	139	106	111	12.8	133	91
M2-6:2 FTS	131	14.2	145	106	124	11.3	136	110	121	14.0	142	94
M2-8:2 FTS	125	20.1	147	89	131	13.9	148	116	129	23.1	149	79
13C-10:2 FTCA	73	23.2	121	49	59	21.2	103	34	52	21.4	93	33
13C2 10:2 FTS	123	18.8	144	88	87	19.6	108	51	108	15.2	133	85
13C2 PFHxDA	101	11.5	120	86	71	13.3	95	58	79	8.6	95	64
13C3 PFBS	109	7.0	118	97	110	8.6	126	96	97	4.2	105	92
13C-6:2 FTCA	52	19.9	98	38	53	9.7	72	40	66	13.7	96	52
13C-6:2 FTUCA	133	11.9	147	116	128	3.5	130	125	127	15.4	146	101
13C-8:2 FTCA	69	19.2	110	48	71	9.7	91	57	64	16.1	88	39
13C-8:2 FTUCA	143	6.0	149	137	136	4.9	139	132	115	15.0	143	91
d7-N-MeFOSE-M	103	10.5	115	86	76	22.1	121	59	74	14.4	105	61
d9-N-EtFOSE-M	107	9.0	118	89	68	29.4	127	45	73	14.7	103	59
d-N-EtFOSA-M	109	8.9	121	92	52	29.8	113	30	70	18.4	102	51
d-N-MeFOSA-M	113	10.5	130	97	64	24.1	112	46	72	18.3	101	52

Table 45-12. In-Stack Detection Limits

Analyte Description	CAS Number	QRL (ng/train)	MDL (ng/train)	QRL (ng/m3)	MDL (ng/m3)	QRL (PPQ)	MDL (PPQ)
Perfluorobutanoic acid (PFBA)	375-22-4	12.60	6.25	4.20	2.08	471.75	234.00
Perfluoropentanoic acid (PFPeA)	2706-90-3	1.80	0.59	0.60	0.20	54.63	17.88
Perfluorohexanoic acid (PFHxA)	307-24-4	2.40	0.92	0.80	0.31	61.24	23.42
Perfluoroheptanoic acid (PFHpA)	375-85-9	1.70	0.62	0.57	0.21	37.42	13.63
Perfluorooctanoic acid (PFOA)	335-67-1	2.50	1.28	0.83	0.43	48.38	24.69
Perfluorononanoic acid (PFNA)	375-95-1	1.50	0.46	0.50	0.15	25.90	7.87
Perfluorodecanoic acid (PFDA)	335-76-2	1.50	0.39	0.50	0.13	23.38	6.02
Perfluoroundecanoic acid (PFUnA)	2058-94-8	2.00	0.99	0.67	0.33	28.41	14.11
Perfluorododecanoic acid (PFDoA)	307-55-1	1.50	0.36	0.50	0.12	19.57	4.67
Perfluorotridecanoic acid (PFTriA)	72629-94-8	1.50	0.35	0.50	0.12	18.10	4.20
Perfluorotetradecanoic acid (PFTeA)	376-06-7	1.50	0.58	0.50	0.19	16.83	6.49
Perfluorobutanesulfonic acid (PFBS)	375-73-5	1.50	0.51	0.50	0.17	40.06	13.62
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	1.50	0.43	0.50	0.14	34.33	9.82
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	1.70	0.82	0.57	0.27	34.05	16.50
Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8	1.50	0.25	0.50	0.08	26.71	4.52
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	2.40	1.06	0.80	0.35	38.46	16.98
Perfluorononanesulfonic acid (PFNS)	68259-12-1	1.50	0.42	0.50	0.14	21.85	6.16
Perfluorodecanesulfonic acid (PFDS)	335-77-3	1.50	0.51	0.50	0.17	20.03	6.86
Perfluorooctanesulfonamide (FOSA)	754-91-6	2.00	0.82	0.67	0.27	32.11	13.23
N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9	2.40	1.21	0.80	0.40	33.67	16.92
N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6	2.40	1.18	0.80	0.39	32.86	16.14
4:2 FTS	757124-72-4	1.50	0.59	0.50	0.20	36.63	14.43
6:2 FTS	27619-97-2	2.00	0.87	0.67	0.29	37.43	16.21
8:2 FTS	39108-34-4	1.70	0.81	0.57	0.27	25.79	12.23
4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	919005-14-4	1.60	0.41	0.53	0.14	33.91	8.61
HFPO-DA (GenX)	13252-13-6	16.60	8.30	5.53	2.77	403.05	201.62
F-53B Major	756426-58-1	1.50	0.51	0.50	0.17	22.57	7.61
F-53B Minor	763051-92-9	1.50	0.55	0.50	0.18	19.00	6.93

RL: Reporting Limit
MDL: Method Detection Limit
PPQ: Parts Per Quadrillion

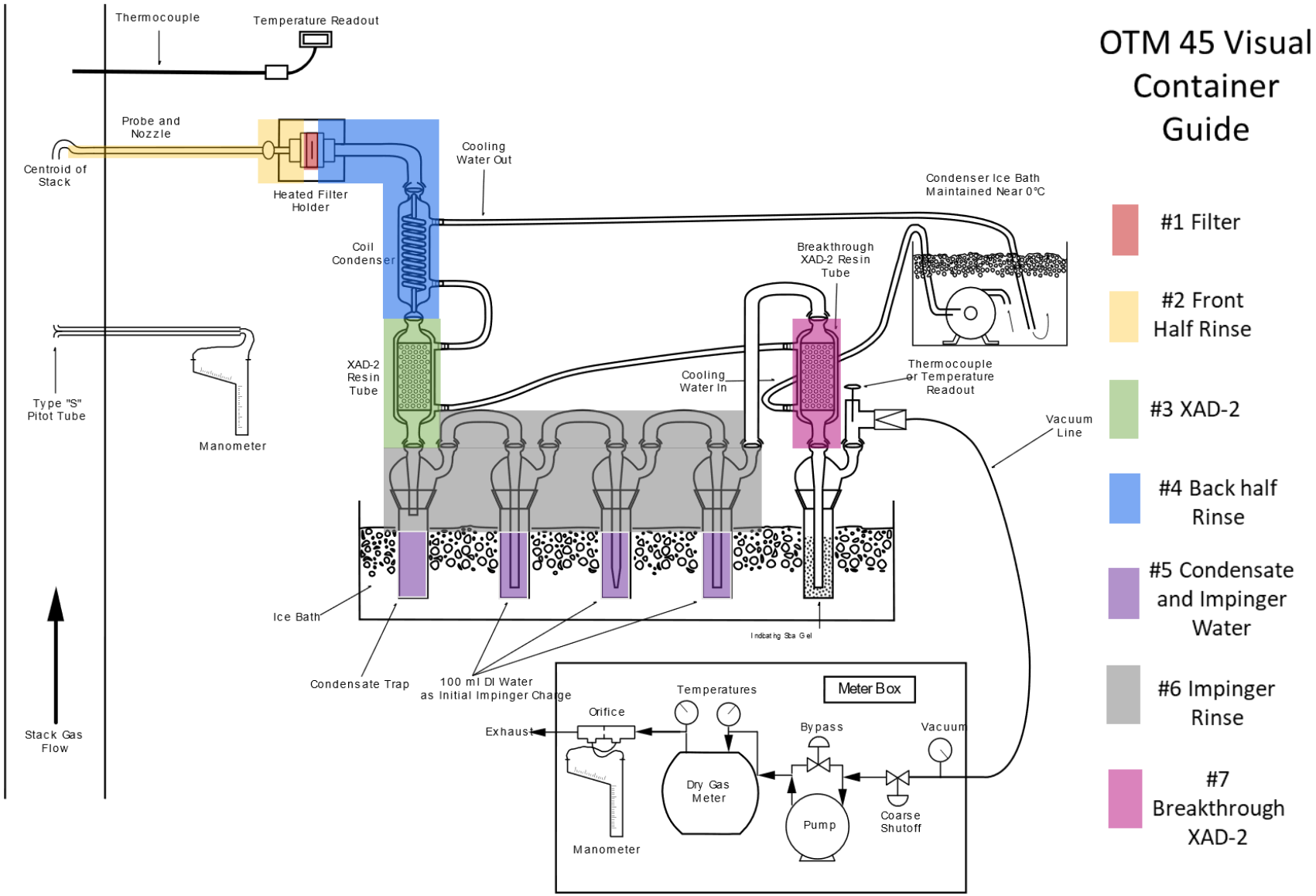
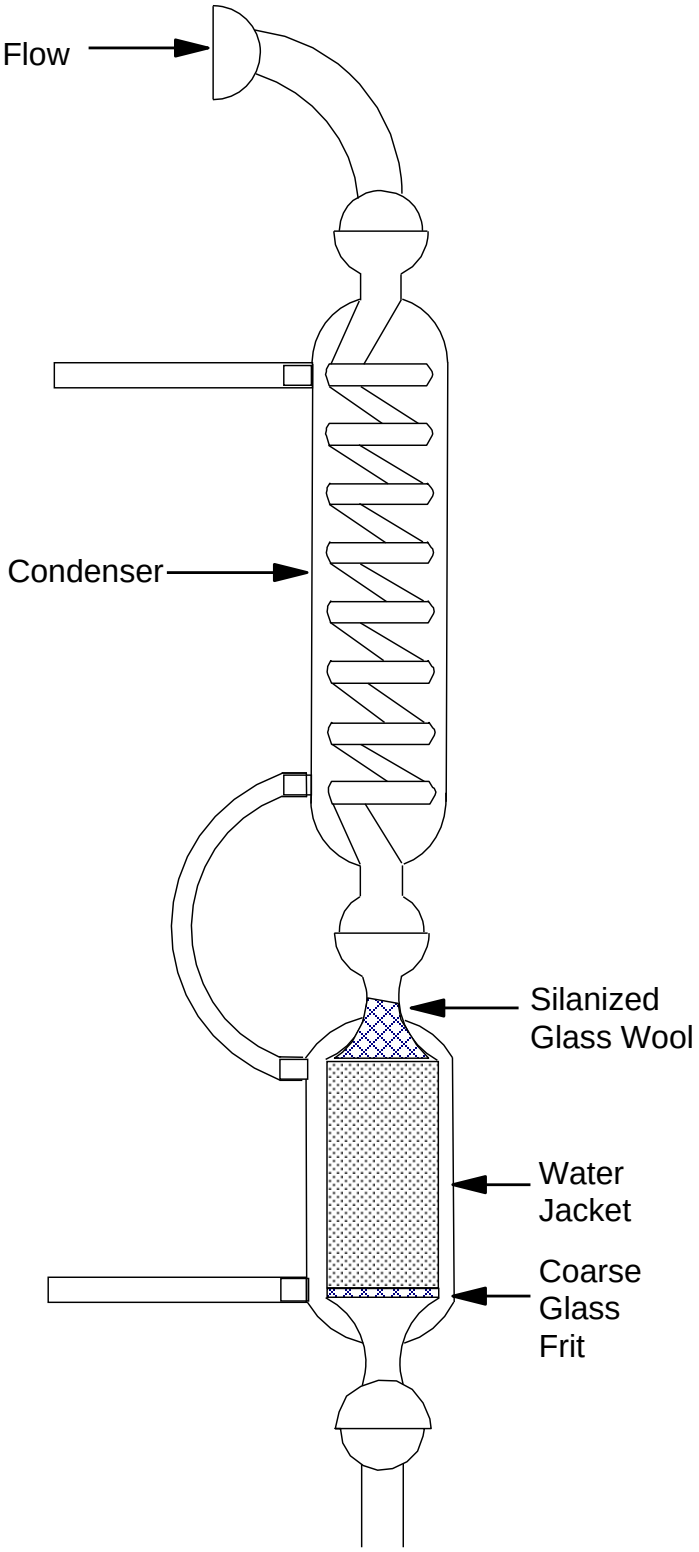


Figure OTM-45-1. Sampling Train


Flow
Condenser
Silanized
Glass Wool
Water
Jacket
Coarse
Glass
Frit

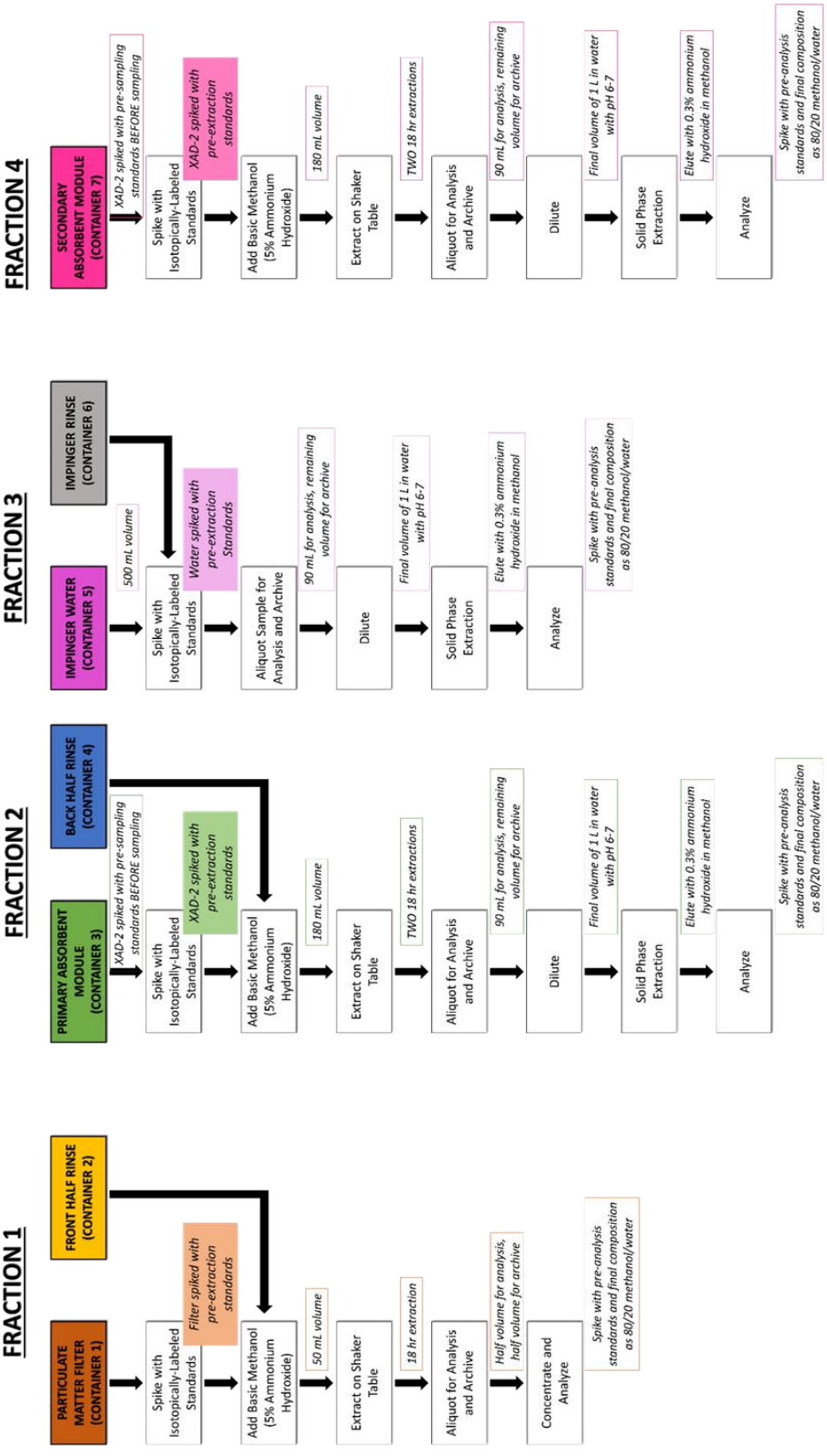


Figure OTM-45–3. Sample Preparation Flow Chart

APPENDIX

PREPARATION OF XAD-2 ADSORBENT RESIN

1.0 Scope and Application

XAD-2® resin, as supplied by the original manufacturer, is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Remove both the salt solution and any residual extractable chemicals used in the polymerization process before use. Prepare the resin by a series of water and organic extractions, followed by careful drying.

2.0 Extraction

2.1 You may perform the extraction using a Soxhlet extractor or other apparatus that generates resin meeting the requirements in Section 9.2.2.1 of OTM-45. Use an all-glass thimble containing an extra-coarse frit for extraction of the resin. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. Because the resin floats on methylene chloride, carefully retain the resin in the extractor cup with a glass wool plug and stainless-steel screen. This process involves sequential extraction with the following recommended solvents in the listed order.

- Water initial rinse: Place resin in a suitable container, soak for approximately 5 min with Type II water, remove fine floating resin particles and discard the water. Fill with Type II water a second time, let stand overnight, remove fine floating resin particles and discard the water.
- Hot water: Extract with water for 8 h.
- Methyl alcohol: Extract for 22 h.
- Methylene chloride: Extract for 22 h.
- Ammonium hydroxide in methanol: Extract for 22 h.

Note: You may store the resin in a sealed glass container filled with ammonium hydroxide in methanol prior to the final extraction.
2.2 You may use alternative extraction procedures to clean large batches of resin. Any size extractor may be constructed; the choice depends on the needs of the sampling programs. The resin is held in a glass or stainless-steel cylinder between a pair of coarse and fine screens. Spacers placed under the bottom screen allow for even distribution of clean solvent. Clean solvent is circulated through the resin for extraction. A flow rate is maintained upward through the resin to allow maximum solvent contact and prevent channeling.
2.2.1 Experience has shown that 1 mL/g of resin extracted is the minimum necessary to extract and clean the resin. The aqueous rinse is critical to the subsequent organic rinses and may be accomplished by simply flushing the canister with about 1 L of distilled water for every 25 g of resin. A small pump may be useful for pumping the water through the canister. Perform the water extraction at the rate of about 20 to 40 mL/min.

2.2.2 All materials of construction are glass, PTFE, or stainless steel. Pumps, if used, should not contain extractable materials.

3.0 Drying

3.1 Dry the adsorbent of extraction solvent before use. This section provides a recommended procedure to dry adsorbent that is wet with solvent. However, you may use other procedures if the cleanliness requirements in Sections 13.2 and 13.14 are met.
3.2 Drying Column. A simple column with suitable retainers, as shown in Figure A–2, will hold all the XAD-2 from the extractor shown in Figure A–1 or the Soxhlet extractor, with sufficient space for drying the bed while generating a minimum backpressure in the column.
3.3 Drying Procedure: Dry the adsorbent using clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. You may use high-purity tank nitrogen to dry the resin. However, you should pass the high-purity nitrogen through a bed of activated charcoal approximately 150 mL in volume prior to entering the drying apparatus.
3.3.1 Connect the gas vent of a liquid nitrogen cylinder or the exit of the activated carbon scrubber to the column by a length of precleaned copper tubing (e.g., 0.95 cm ID) coiled to pass through a heat source. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C.
3.3.2 Allow the solvent to drain from the resin prior to placing the resin in the drying apparatus.
3.3.3 Flow nitrogen through the drying apparatus at a rate that does not fluidize or agitate the resin. Continue the nitrogen flow until the residual solvent is removed.
Note: Experience has shown that about 500 g of resin may be dried overnight by consuming a full 160-L cylinder of liquid nitrogen.

4.0 Quality Control Procedures

4.1 Report quality control results for the batch. Re-extract the batch if the residual extractable organics fail the criteria in Section 9.
4.2 Residual Quality Check. If adsorbent resin is cleaned or recleaned by the laboratory, perform a quality control check for residual PFAS. Analyze a portion of each batch of cleaned XAD-2 as you would a laboratory sample matrix blank (LSMB) in OTM-45. If the adsorbent exceeds the QC criteria the batch must be re-extracted with 4 % ammonium hydroxide in methanol, dried and reanalyzed.

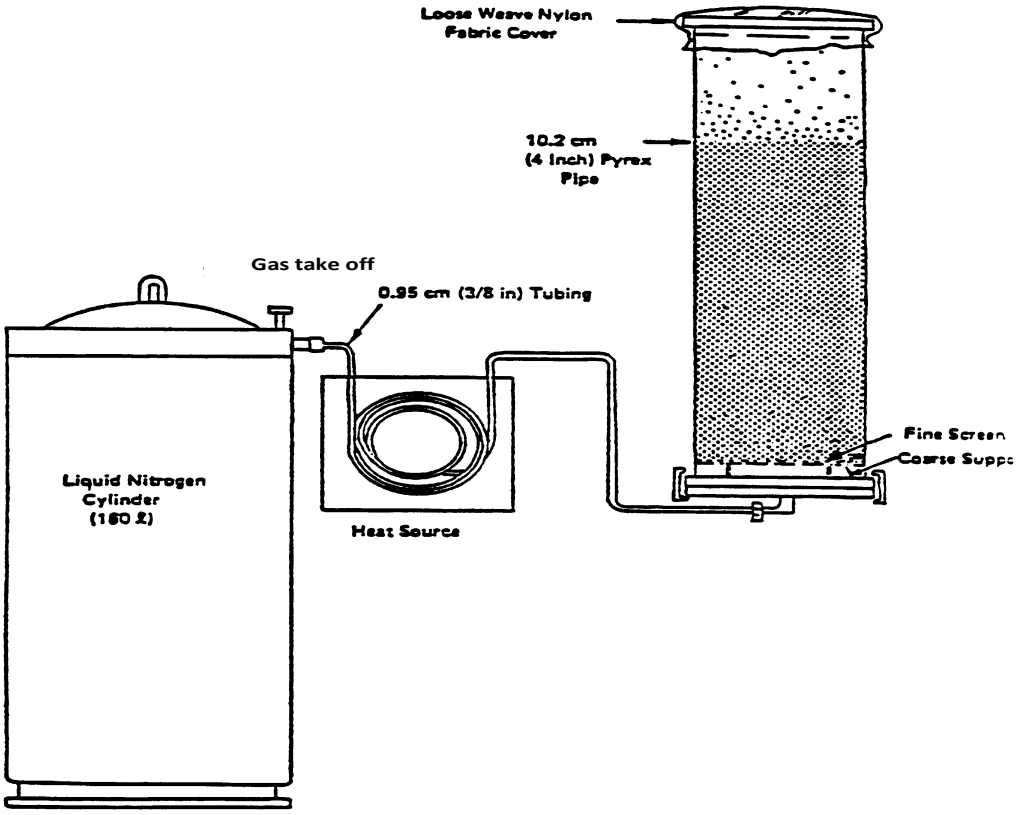


Figure A–1. XAD-2 fluidized-bed drying apparatus.