

## **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 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 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 recommends 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 emitted 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 monitoring applications, which include the analysis of multiple short-chain PFAS that cannot be measured by EPA Method 537.1. 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 or a state 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 more data from stakeholders becomes available. Due to the urgent 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 any and all feedback, comments, and additional data coming from the application of this method as we work to adjust this method in anticipation of developing a reference method for PFAS from air emission sources. PFAS compounds encompass a wide variety of moiety’s that can lead to different physical and chemical properties. As such this method may not be suitable for certain PFAS compounds with unique properties, requiring evaluation of this method for PFAS compounds that might be added later.

**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 (Mail Code E143-02)  
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## **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 (Boiling point > 100°C) and particulate-bound 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 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 should 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 should 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 isotope spike standards and the pre-analysis isotope spike standards specified in the method must be used. Users may modify the method to 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 compounds in source emissions. Gaseous 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 extract fractions 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, exclusively applied to the pre-extraction 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 particle or vapor 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. Use alternative recovery standards to assess the recovery of a compound class relative to a step in the sampling and analysis procedure that is not already assessed as a mandatory part of this method.

3.2 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.

3.3 Batch Blank Sample. A laboratory blank sample composed of a precleaned filter and XAD-2 media processed and analyzed using the same procedures as a field sample.

3.4 Calibration Standard. A solution of the method analytes, pre-extraction standards, and pre-analysis standard(s) prepared from the Primary Dilution Standards and stock standards. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.5 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.

3.6 Congener. An individual compound with a common structure, only differing by the number of fluorine atoms attached to the structure.

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

3.8 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 and procedures.

3.9 Homolog. A compound belonging to a series of compounds with the same general molecular formula, differing from each other by the number of repeating units.

3.10 Pre-extraction Standards. Pre-extraction standards are isotopically labeled analogues of the method analytes that are added to the sample prior to extraction in a known amount.

Note: Not all target PFAS currently have an isotopically labeled analogue. In these cases, an alternate isotopically labelled analogue (isotopologue) is used as recommended in Table 45- 1.

3.11 Branched and linear isomers. Individual compounds with a common molecular formula, differing by the position of carbon and fluorine atoms attached to the structure.

3.12 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, added to the original sample in a known amount and carried through the entire analytical procedure.

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

3.14 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 to which known quantities of the method analytes and isotope dilution analogues are added. The results of the LFMB verify method performance in the absence of sample matrix.

3.15 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.

3.16 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 Perfluorinated alkyl substances. Aliphatic substances where all of the hydrogen atoms attached to carbon atoms have been replaced by F atoms, except those H atoms whose substitution would modify the nature of any functional groups present.

3.18 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.

3.19 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 ( $[M - H]^-$ ) of the method analyte, except for HFPO-DA. For this analyte, the precursor ion is formed by decarboxylation of HFPO-DA.

3.20 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 two isotopically labeled analogues of the method analytes. 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 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 fraction: (i.e., the primary and secondary XAD-2 adsorbent traps, filter, and impinger samples) and to laboratory blanks immediately before extraction. Used to correct the quantity of the native target compounds present in the sample for extraction, cleanup, and concentration recovery.

Note: Not all target PFAS currently have an isotopically labelled analogue. In these cases, an alternative isotopically labelled analogue is recommended in Table 45-1.

3.24 Pre-sampling Standard(s). A group of isotopically labeled compounds added in a known amount to the XAD-2 adsorbent prior to sampling used to indicate the sample collection and recovery efficiency of the method.

3.25 Pre-transport Standard(s). A group of isotopically labeled compounds added by the laboratory into the sample containers used in the field to contain and transport probe rinse and impinger samples. The measured concentration of the pre-transport recovery standard provides a

quality check on potential probe rinse sample spillage or mishandling after sample collection and during shipping.

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

3.27 Quality Control Standard (QCS). A calibration standard prepared independently from the primary 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 is to verify the integrity of the primary calibration standards.

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

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

3.30 Sampling Train Field Blank (STFB). The complete field assembly and recovery of an OTM-45 sampling train without actual sampling, including 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.

3.31 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 STFB 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.

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

3.33 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 method detection limit (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.

#### *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 batch blank samples. Use high purity reagents, solvents, and standards to minimize interference problems in sample analysis.

Note: In this method,  $^{13}\text{C}_3$ -PFBA is used as a pre-analysis standard(s) and  $^{13}\text{C}_4$ -PFBA is used as an isotope dilution analogue. Both share the same product ion, m/z 172. Because the natural abundance of  $^{13}\text{C}$  is 1.1%, there is a 1.1% contribution to the  $^{13}\text{C}_4$ -PFBA area from the lone, unlabeled  $^{12}\text{C}$  atom in  $^{13}\text{C}_3$ -PFBA. Users of this method may consider this bias to the area of the PFBA isotope dilution analogue insignificant.

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 the product 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 in contact with any glass containers or pipettes as PFAS analytes 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 Isotopic purity of  $^{13}\text{C}$ -PFBA. In this method,  $^{13}\text{C}$ -PFBA is used as a pre-analysis standard(s) and  $^{13}\text{C}$ -PFBA is used as an isotope dilution analogue. Both share the same product ion,  $m/z$  172. Ten nanograms per liter of  $^{13}\text{C}$ -PFBA is added to the sample prior to extraction (10 ng/mL extract concentration assuming 100% recovery), and 10 ng/mL of  $^{13}\text{C}$ -PFBA is added to the final extract. Because the natural abundance of  $^{13}\text{C}$  is 1.1%, there is a 1.1% contribution to the  $^{13}\text{C}$ -PFBA area from the lone, unlabeled  $^{12}\text{C}$  atom in  $^{13}\text{C}$ -PFBA. The authors confirmed this contribution empirically. Users of this method may consider this bias to the area of the PFBA isotope dilution analogue insignificant.

4.7 Isotopic purity of  $^{13}\text{C}$ -PFBA. A trace amount of  $^{13}\text{C}$ -PFBA was detected in the  $^{13}\text{C}$ -PFBA. The contribution was no greater than 1%. The contribution of the pre-analysis standard(s) to the isotope dilution analogue is insignificant.

4.8 Telomer Sulfonates. Each of the three telomer sulfonates in the analyte list (4:2FTS, 6:2FTS, and 8:2FTS) are referenced to their  $^{13}\text{C}$  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 ( $^{34}\text{S}$ ) at 4.25%. Thus, the precursor ions of the  $^{13}\text{C}_2$  isotopically labeled analogues and the naturally occurring  $^{34}\text{S}$  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  $^{34}\text{S}$  analogue of the native telomer sulfonates. At the concentrations used in this study, the contribution of the  $^{34}\text{S}$  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 strict safety program for the handling of PFAS samples to avoid contact with sampling media and sample recovery solutions.

5.1 Selected PFAS compounds, namely PFOS and PFOA have known aneugenic, endocrine, and teratogenic effects in laboratory animal studies. Be aware of the potential for inhalation, skin absorption and ingestion exposure to field personnel and laboratory analysts.

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.

5.4 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. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment is identical to that used in EPA Method 5 determinations. The OTM 45 sampling train is very similar, but not identical to the SW-846 Method 0010 sampling train. The specific OTM 45 adaptations are: the use of condenser and XAD-2 adsorbent module, which are used for the primary capture of PFAS compounds that pass through the glass or quartz-fiber filter in the gas phase; a series of impingers for additional capture of PFAS compounds that pass through the primary XAD-2 adsorbent module; and a secondary XAD-2 adsorbent module which is to determine the breakthrough of PFAS compounds not captured by the primary XAD-2 adsorbent module and impingers. The train is identical to that described in section 6.1.1 of Method 5 of appendix A-3 to 40 CFR part 60 with the following additions:

6.1.1 Nozzle. The nozzle must be made of quartz or borosilicate glass or titanium. Stainless steel nozzles should 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  $120 \pm 14$  °C ( $248 \pm 25$  °F) during sampling. Use a PTFE ferrule or single-use PTFE coated O-ring 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).

6.1.3 Filter Holder. Use a filter holder of borosilicate glass with a PTFE frit or PTFE-coated wire filter support. The holder design should provide a positive seal against leakage from the outside or around the filter. The holder should 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 must be evaluated for PFAS contamination.

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  $120 \pm 14$  °C ( $248 \pm 25$  °F) during sampling or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.5 Filter Temperature Sensor. Install a temperature sensor capable of measuring temperature to within  $\pm 3$  °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 filter. Encase the sensing tip of the sensor in glass or PTFE if needed.



6.1.6 Sample Transfer Line. The sample transfer line transports gaseous emissions from the heated filter holder to the condenser and must be heat traced and constructed of glass or PTFE with connecting fittings that form leak-free, vacuum-tight connections without using sealing greases or tapes. PFA tubing may also be used for the sample transfer line. Keep the sample transfer lines as short as possible and maintain the lines at a temperature of  $120\text{ }^{\circ}\text{C} \pm 14\text{ }^{\circ}\text{C}$  ( $248\text{ }^{\circ}\text{F} \pm 25\text{ }^{\circ}\text{F}$ ) using active heating when necessary. 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.

Note: The use of a sample transfer line should be avoided if possible. If a sample transfer line is used, it must be evaluated for PFAS contamination.

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. Typically, a submersible pump is placed in the impinger ice water bath to circulate the ice water contained in the bath. Verify the function of this system by measuring the gas temperature at the entrance to the adsorbent module. Maintain this temperature at  $< 20\text{ }^{\circ}\text{C}$  ( $68\text{ }^{\circ}\text{F}$ ).

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 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 an optional 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 0.5g.

6.2.6 Aluminum Foil. Use heavy duty aluminum foil cleaned by rinsing three times with 5% ammonium hydroxide in methanol 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 glass serological pipettes typically 150 mm long x 6 mm ID.

## 6.5 Solid Phase Extraction (SPE)

6.5.1 SPE Cartridge. (Waters OASIS WAX 500mg/6 cc, Waters Corporation, Milford, MA or equivalent) SPE cartridges containing weak anion exchange, mixed-mode polymeric sorbent (polymeric backbone and a diamino ligand), particle size approximately 33 µm. The SPE sorbent

must have a pKa above 8 so that it remains positively charged during extraction. SPE cartridges containing 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 should be sealed while in storage to prevent ambient contamination of the SPE sorbent.

6.5.2 Vacuum Extraction Manifold. Equipped with flow and vacuum control [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 (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 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. These modifications were not used on the LC system used for method development. However, 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 3 µm 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 in order to construct calibration curves and calculate analyte concentrations using the internal standard 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* (see <https://pubs.acs.org/isbn/9780841230460>) of the American Chemical Society (ACS) Committee on Analytical Reagents 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 fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles.

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 this method 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 the 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 batch blank conducted on a filter and adsorbent lot combination used for a test can serve this purpose.

7.1.3.1 Storage. Store adsorbent in its original purchase container, a clean wide-mouth HDPE container with a polypropylene or polyethylene-lined cap, or in 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 5% ammonium hydroxide in methanol, drying in a 110 °C (230 °F) oven, and storing in a 5% ammonium hydroxide in methanol 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 5% ammonium hydroxide in methanol-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. As an alternative, use other types of desiccants (equivalent or better), subject to the approval of the Administrator.

## 7.2 Sample Recovery Reagents.

7.2.1 Methanol. CH<sub>3</sub>OH, CASRN 67-56-1, LC grade (Fisher Scientific, Cat. No. A456 or equivalent).

7.2.2 Ammonium hydroxide solution.  $\text{NH}_4\text{OH}$ , CASRN 1336-21-6, approximately 56.6% in water as ammonium hydroxide (w/w), approximately 28% in water as ammonia, approximately 14.5 N (Fisher Scientific, Cat. No. A669, Certified ACS Plus grade, or equivalent).

7.2.3 Ammonium hydroxide, 5% in methanol rinsing solution. Prepared by diluting of 50 mL ammonium hydroxide solution into 1 L final volume in methanol.

### 7.3 Sample Extraction and Cleanup Reagents.

7.3.1 Ammonium hydroxide 5% in methanol extraction solution. (methanol / 5%  $\text{NH}_4\text{OH}$ ).

Prepared by diluting of 50 mL ammonium hydroxide solution into 1 L final volume in methanol (see Section 7.2). This reagent is added to methanolic solutions of PFAS to prevent esterification.

7.3.2 Ammonium hydroxide, 0.3%, in methanol (SPE extraction solution). Prepared by diluting 12 mL of ammonium hydroxide into 4L of methanol.

7.3.3 Sodium Hydroxide ( $\text{NaOH}$ ), 0.1 N, in water. Prepared by diluting 400 mL of 1N  $\text{NaOH}$  in 3.6L of water for a total volume of 4L.

7.3.4 Hexane. Reagent grade.

### 7.4 Standard Solutions

#### 7.4.1 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 (amu). It is necessary to include ammonium hydroxide in solutions of both isotopically labeled and native analytes. The amount of ammonium hydroxide needed may be calculated using the following equation:

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

#### 7.4.2 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.

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.

7.4.3 Storage Temperatures for Standard Solutions. Store stock standards at less than 4 °C unless the vendor recommends otherwise. The Primary Dilution Standards (PDS) may be stored at any

temperature, but cold storage is recommended to prevent solvent evaporation. PDS stored at  $-20^{\circ}\text{C}$  showed no change in analyte concentrations over a period of 6 months.

7.4.4 Pre-analysis standard(s). Obtain the pre-analysis standard(s) as certified standard solutions, if available, or as the neat compounds. Note that Chemical Abstracts Registry Numbers are not currently available for these compounds. All the pre-analysis standard(s) listed in this section must be used. 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 were fortified with  $10\ \mu\text{L}$  of the pre-analysis standard(s) to yield a concentration of  $10\ \text{ng/mL}$  for  $^{13}\text{C}_3\text{-PFBA}$  and  $^{13}\text{C}_2\text{-PFOA}$ .

7.4.5 Pre-analysis primary dilution standard (pre-analysis standard(s)-PDS). Prepare the pre-analysis standard(s)-PDS in methanol and add ammonium hydroxide if not already present to prevent esterification. The PDS concentrations for the method are listed in the Table 45-3

7.4.6 Pre-extraction Standards. Obtain the isotopically labeled analogues listed in Table 45-1 as individual certified standard solutions or as certified standard mixes. All listed isotope dilution analogues must be used, if available. Linear isomers are recommended to simplify peak integration.

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

Note: Pre-extraction standard(s) is identical to Isotope Dilution Analogues in Method 533

7.4.7 Pre-extraction Primary Dilution Standard (pre-extraction standards -PDS). Prepare the pre-extraction standards - PDS in methanol and add ammonium hydroxide if not already present to prevent esterification as described in Section 7.4.1. The final extracts are fortified with 10 µL of the PDS to yield concentrations of 40 – 160 ng/sample fraction. Note that the concentrations of sulfonates in the pre-extraction standards PDS is based on the weight of the salt. It is not necessary to account for difference in the formula weight of the salt compared to the free acid for sample quantitation.

7.4.8 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 methanol containing 4 mole equivalents of ammonium hydroxide, as described in Section 7.4.2. Technical grade, quantitative PFHxS and PFOS standards containing branched and linear isomers must be used when available.

7.4.9 Correction for Analytes Obtained in the Salt Form. This method measures all forms of the analytes as anions while the identity of the counterion is inconsequential. 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.

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

7.4.10 Analyte PDS. The analyte PDS is used to prepare the calibration standards and to fortify the laboratory fortified blanks, laboratory fortified sample matrix spikes, laboratory fortified sample matrix spike duplicates (LFMB s, LFSMs and LFSMDs) 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.

7.4.11 Calibration Standards. Prepare a series of calibration standards of at least five levels by diluting the analyte PDS into methanol containing 20% reagent water. 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 nominal concentrations of the pre-extraction standards can be 40 ng/mL in the extract for 4:2FTS, 6:2FTS and 8:2FTS, and 10

ng/mL for all others. The analyte calibration ranges from approximately 0.50 ng/mL to 25 ng/mL extract concentration.

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

7.6 Argon. Used as collision gas in MS/MS instruments. Argon should 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 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 batch blank criteria in Section 13.2 of this method is acceptable.

8.1.1.1.1 Soak all glassware in hot soapy water (Alconox® 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, dichloromethane, and 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 Rinse glassware immediately before use with 5% ammonium hydroxide in methanol.

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 repeat the cleaning procedures in Section 8.1.1.1 of this method.

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. Follow the XAD-2 with cleaned glass wool and tightly cap both ends of the module.

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 DL 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 once during each test run.

8.1.3 Preparation of Sampling Train. Do not use sealing greases 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, you must wrap the module with aluminum foil or 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. Clean and prepare a complete set of sampling train components that will contact the sample for each sampling run. Include at least one complete field test proof blank and at least one field test field blank, as described in Sections 9.1.3 and 9.1.4 of this method.

8.1.3.2 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.

8.1.3.3 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.

8.1.3.4 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.

8.1.3.5 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. Ensure proper temperature of the gas entering the adsorbent module before proceeding.

8.1.4 Leak-Check Procedure. 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. 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. 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) should not be exceeded.

8.1.5.2 XAD-2 Adsorbent Module Temperatures. During testing, 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 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. Conduct a post-test leak check. Remove the probe from the train and close off both ends. Seal off the inlet to the filter. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the primary sorbent module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module. Cap the filter-holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section. Cap all sorbent module openings. Disconnect the

sorbent module knockout trap from the impinger train inlet and cap both of these openings. Ground-glass stoppers, Teflon tape, or other inert materials such as cleaned aluminum foil (e.g., rinsed with 5% ammonium hydroxide in methanol rinsing solution) may be used to seal all 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. To avoid sample contamination and unnecessary exposure to toxic chemicals, smoking or eating in the sample recovery area shall not be allowed. Inspect the train prior to and during disassembly. Note and record any abnormal conditions (e.g., broken filters, colored impinger liquid). Recover and prepare samples for shipping as follows in Sections 8.2.4 through 8.2.12 of this method.

8.2.3 Moisture Weight. Weigh the adsorbent module, impingers, and silica gel impinger to within  $\pm 0.5$  g using the field balance and record the weights. This information is required to calculate the moisture content of the effluent gas.

Note: Moisture measurement in the field using the OTM 45 train requires weighing the primary adsorbent module 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 Container No. 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 dry inert bristle brush and a sharp-edged blade. Seal the container and store in a thermally insulated container for transport to the laboratory.

8.2.5 Container No. 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 the 5% Ammonium hydroxide in methanol rinsing solution. 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.

8.2.6 Container No. 3 – Primary Adsorbent Module Sample. Remove the module from the train and tightly cover both ends. Replace the retaining clips around the glass joint. Remove the foil, drain the recirculating water from the module, weigh and record the module weight. The adsorbent trap module should be used as a sample transport container. Both ends should be sealed with tightly fitting ground-glass stoppers followed by Teflon tape around the glass joint. The sorbent trap should then be labeled, re-covered with aluminum foil, and packaged on ice for transport to the laboratory.

Note: The XAD-2 resin modules (primary and breakthrough) 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 module as a separate fraction may change.

8.2.7 Container No. 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 5%

ammonium hydroxide in methanol rinsing solution. Collect all the rinses in the HDPE sample bottle and label as Container No. 4. Mark the level of the liquid on the container. Store the sample container refrigerated or on ice until laboratory shipment.

8.2.9 Container No. 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.

Note: Make sure that no ammonium hydroxide in methanol rinsing solution is transferred to the container No. 5 sample. Doing so may compromise the sample for analysis.

8.2.10 Container 6 – Impingers Rinse. Rinse impingers 1-4 three times with the 5% ammonium hydroxide in methanol rinsing solution. 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. If impingers are used in a subsequent sampling run they must be rinsed three times with reagent water to remove residual ammonium hydroxide in methanol.

8.2.11 Container 7 – Secondary Adsorbent Module Sample. Remove the module from the train and tightly cover both ends. Replace the retaining clips around the glass joint. Remove the foil, drain the recirculating water from the module, weigh and record the module weight. The adsorbent trap module should be used as a sample transport container. Both ends should be sealed with tightly fitting ground-glass stoppers followed by Teflon tape around the glass joint.

The sorbent trap should then be labeled, re-covered with aluminum foil, and packaged on ice for transport to the laboratory.

8.2.10 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.

8.2.11 Field Sample Handling, Preservation, Storage, and Transport. Store all field samples, with the exception of the particulate filter, temporarily on ice (approximately 4°C) and dark conditions prior to transport to the laboratory. The particulate filters should be shipped in a thermally insulated container and may remain unrefrigerated. Ship samples on ice, shielded from ultraviolet light. The particulate filters should be shipped unrefrigerated. 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 Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward.

8.2.12 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 but not longer than 28 days from date of collection

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 Samples must be extracted within 28 days of collection. Extracts are stored at room temperature and must be analyzed within 28 days of extraction.

8.3.6 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 media blank (i.e., batch blank) 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.

QC procedures include the Initial Demonstration of Capability (IDC) and ongoing quality control (QC) requirements. This section describes each QC parameter, its required frequency, and the performance criteria that must be met in order 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 8.4 and 9.2 of Method 5 of appendix A-3 to 40 CFR part 60.

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. Analysis of the FSMBs should be compared to the background level criteria in 9.2.2.1. Failure to meet these

levels does not invalidate data. However, the measured target compound mass in each fraction will need to be reported and used to interpret sample results.

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 sample train proof blank for each test series at a single facility. A sample train proof blank train 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 proof blank train 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 proof blank train 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 field train proof blank assessment samples. Failure to meet these levels does not invalidate data. However, the measured target compound mass in each fraction will need to be reported and used to interpret sample results

9.1.4 Sample Train Field Blank. STFBs must be submitted with the samples collected at each sampling site. At a minimum, conduct at least one sample train field blank for each test series at a single facility. A sample train field blank train consists of a fully assembled train at the sampling site using glassware that has been previously used for sampling. Prepare and assemble the proof blank train in a manner identical to that described in Section 8.1.3 and 8.1.4 of this method. The STFB 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 proof 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 for field train proof blank assessment samples. Failure to meet these levels does not invalidate data.

However, the measured target compound mass in each fraction will need to be reported and used to interpret sample results.

9.1.5 Pre-sampling Standard Recoveries. Pre-sampling standard XAD-2 adsorbent spike recoveries must demonstrate on a per sample basis that recovery of the labeled standards achieve the requirements in Table 45-5 of this method. Recoveries below the acceptable range of 70-130% for the pre-sampling standard spikes may require a root cause evaluation of the cause for poor recovery. 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.

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

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

BT should be less than 30%. For any BT greater than 10%, add the Fraction 4 mass to the total sample mass for emissions calculations. Failure to meet breakthrough requirements may invalidate reported results and require repeat sampling.

## 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 estimated detection limit.

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 blank 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 fulfil this requirement.

9.2.1.3 Initial MDL Determination. Perform an MDL determination for each sample media fraction (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 media by spiking each media 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 less than 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.

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:

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

Where,

S = the standard deviation

3.963 is a constant value for seven replicates<sup>1</sup>

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

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

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

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 (Sect. 9.2.2.12) to confirm the accuracy of the primary calibration standards.

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 established in Section 9.2.1.3. Ideally, estimated quantitative limits, and therefore acceptable blank and background levels, should be below the established MDLs, but no greater than the MDL.

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 below one third of the established MDLs, but no greater than the MDL. If levels are found above the MDL, further clean the sampling media until levels are below MDL.

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 below the established MDLs, but no greater than the MDL. If method analytes are detected in the LSMB at concentrations greater than or equal to this level the results should be flagged accordingly. Resolve the source of contamination before proceeding with additional analyses.

#### 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 background contamination can be a significant problem, some MDLs may be background limited.

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 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.

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 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.

9.2.2.4 Laboratory Fortified Media Blanks. 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.

9.2.2.4.2 Evaluate Analyte Recovery. Calculate the percent recovery (%R) using the equation:

$$\%R = \frac{(A-B)}{C} \times 100 \quad \text{Eq. 45-7}$$

Where,

A = measured concentration in the fortified sample,

B = measured concentration in the unfortified sample, and

C = fortification concentration.

Note: In order 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.

9.2.2.5 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) (as indicated by peak area) 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) standard 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.  
extract.

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 20-130% recovery requirements summarized in Table 45-5. Calculate the percent recovery (%R) for each analogue as follows:

$$\%R = \frac{\text{Measured Concentration of the Pre-extraction Isotope analogue}}{\text{Fortification concentration of the Pre-extractoin Isotope analogue}} \times 100 \quad \text{Eq. 45-8}$$

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 should 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 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 recovery criterion, prepare fresh standard dilutions and repeat the Calibration Verification.

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

9.4.2 Field sample volume.

9.4.3 Field sampling date.

9.4.4 Extraction dates.

9.4.5 Analysis dates and times.

9.4.6 Analysis sequence/run chronology.

9.4.7 Quantitation Reports.

## *10.0 Calibration and Standardization*

10.1 Sampling System. Same as Sections 6.1 and 10.1 through 10.7 of Method 5 of appendix A-3 to 40 CFR part 60.

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 instrument manufacturer's guidance. Optimization may be performed at analyte concentrations of 1.0  $\mu\text{g/mL}$ . 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 two pre-analysis standard(s) that are used as reference compounds for the internal standard quantitation of the pre-extraction standards. The pre-extraction standards are used as reference compounds to quantitate the native analyte concentrations. The pre-extraction standard references 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 not be within two 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: Forcing the calibration curve through the origin may improve the estimate of the background levels of method analytes which are an important consideration for this method.

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 MDL 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 two 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 80 percent methanol/water. 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 45-4 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 FH Rinse (Containers 1 and 2). Place the particulate filter into an appropriate size HDPE bottle. Spike the filter with the appropriate pre-extraction recovery standard solution. Add front-half sample rinsate (Container 2) to each respective filter container. If there is less than 50 mL of rinsate, add extraction solvent for a total of 50 mL. Extract samples on a shaker table for a minimum of 18 hours. Measure and record the final volume. After extraction, the solvent is divided: half of the volume used in the extraction is measured for concentration; the remaining portion is archived. This is achieved by filtering into separate, appropriately sized HDPE containers by placing a filter paper in a disposable polypropylene funnel and pouring the sample extracts through the funnels and into the HDPE containers.

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

11.1.2.1 Spike the XAD-2 in the module with the appropriate pre-extraction recovery standard solution (Table 45-3). Empty the module contents into an HDPE wide mouth bottle. Rinse the inside of the module with 5% ammonium hydroxide in methanol 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 5% ammonium hydroxide in methanol for a total of 180 mL. If there is excess rinsate, you may add up to half of the volume and save the remaining half for the second extraction described in 11.1.2.5.

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

11.1.2.4 Decant the 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 sample rinsate remaining, add 5% ammonium hydroxide in methanol for a total of 180 mL. Extract the sample a second time on a shaker table for a minimum of 18 hours. After the second extraction is completed, the extraction solvent is decanted into the container with the first extract leaving the XAD-2 in the extraction container. Measure and record the final volume. Divide extract with half of the volume going for concentration (Section 11.2) and archive the remaining half.

11.1.3 Fraction 3 Condensate/Impinger Water and Impinger Rinses (Containers 5 and 6). The sample is brought up to 500 mL in a Nalgene 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). Spike each sample with 1.0 mL of the IDA solution. The water sample is divided: 250 mL (or half the sample if more than 500 mL was received) is measured for analysis in an appropriately sized Nalgene bottle; the remaining half is archived in an appropriately sized Nalgene bottle.

11.1.3.1 Solid Phase Extraction (SPE) of Aqueous Samples. Wash the SPE cartridges with 5.0 mL 0.3% NH<sub>4</sub>OH/methanol. Wash with 5.0 mL of 0.1 N NaOH/water. Close valve when ~ 200 uL remains on top to keep columns wet. After this step, ensure the columns do not go dry until the completion of loading and rinsing samples. Label and add the reservoir to the column. Add sample to the column. Using a vacuum, pull the entire sample through the cartridge at a rate of 2-5 drops per second. After the entire sample has been loaded onto the column, rinse the Nalgene bottle twice with 5 mL of reagent water and pour onto the column reservoir. After the final loading of the sample but before completely passed through the cartridge, allow the column to dry well with vacuum for 15 minutes.

11.1.3.2 SPE Column Wash with Hexane. Load 5 mL of hexane to the column and soak for five minutes. Elute to waste. Load an additional 5 mL of hexane and elute to waste without a soaking period. Allow the column to dry completely with vacuum for 5 to 10 minutes.

11.1.3.3 SPE Elution. Rinse Nalgene bottle with 4 mL of 0.3% NH<sub>4</sub>OH/methanol. Pour rinse into the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into a polypropylene container large enough to contain volume from 11.1.3.4. Repeat rinse with an additional 4 mL of 0.3% NH<sub>4</sub>OH/methanol. The total collection should be approximately 8 mL. Measure and record the final volume.

11.1.3.4 Combine with Container 6 (Impinger Rinse). Measure and record the Container 6 rinse volume. Transfer half to a HDPE container for sample archive. Combine with half of the SPE eluent. Cap, seal with Teflon tape, mark the level and store refrigerated at approximately 4 °C. Combine the remaining Container 6 rinse with the remaining SPE eluent and concentrate as described in 11.2.

11.1.3.4 Final volume for extract. Add 0.5 mL of IS 50 ng/mL concentration and 2 mL of water to the extract. This will create an extract with a final solvent composition of 80:20 methanol:water. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial. Archive the rest of the extracts for re-injection and dilution. Seal the vial with a polypropylene screw cap.

11.1.4 Fraction 4 Breakthrough 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 5% ammonium hydroxide and add to HDPE bottle.

11.1.4.2 Add 5% ammonium hydroxide in methanol for a total volume of 180 mL

11.1.4.3 Extract the samples on a shaker table for a minimum of 18 hours.

11.1.4.4 Decant the extraction solvent into an HDPE container leaving the XAD-2 in the extraction container.

11.1.4.5 Add 180 mL of 5% ammonium hydroxide in methanol to the XAD extraction container. Extract the sample a second time on a shaker table for a minimum of 18 hours. After the second extraction is completed, the extraction solvent is decanted into the container with the first extract leaving the XAD-2 in the extraction container. Divide extract with half of the volume going for concentration (Section 11.2) and archive the remaining half.

11.2 Sample Concentration

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11.2.1 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 5% ammonium hydroxide in methanol and add to digestion vessel. Cover each vessel with a ribbed polypropylene watch glass.

11.2.1.1 To accommodate large volumes, the extract and rinsate can either be concentrated in multiple digestion vessels until concentrated to a level that allows recombination (with proper rinsing) OR additional extract can be added to a digestion vessel as volume is reduced during the concentration step. Concentrate the sample to below 10 mL, but not to dryness. Transfer to a 10 mL polypropylene tube, rinsing the digestion vessel adequately.

11.2.2 Blow down remaining volume to below 2 mL, but not to dryness, with an N-EVAP at 55-60 °C. Bring up volume to 2 mL with DI water or 5% ammonium hydroxide in methanol. Cap snugly and ensure there are no leaks. Store refrigerated at approximately 4 °C until analysis. Analyze within 28 days of extracting.

### 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 (or FD)). 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 at or below the QRL. 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 may indicate that recalibration is required 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

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

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

$C_{is}$  = the concentration of the pre-extraction isotopically labeled standard (pg/ $\mu$ L).

$C_s$  = the concentration of the native compound in the continuing calibration standard (pg/ $\mu$ L).

$A_i$  = Integrated ion current for the isotopically labeled compound.

$A_n$  = Integrated ion current for the target native compound.

$C_i$  = The concentration of the labeled compound used to perform isotope recovery correction, pg/ $\mu$ L.

$C_n$  = The concentration of the target native compound, pg/ $\mu$ L.

$C_{ndscm}$  = 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,  $\mu$ L.

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 comparison of its retention time with that of the corresponding analyte peak in an initial calibration standard or CCC.

12.3.2 Qualitative Identity by Confirming the Parent and Product ions. Confirm that the native and pre-extraction isotope parent 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  $\pm 6$  scans or  $\pm 6$  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, 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.

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

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 native standards and isotopically labeled analogs are not currently available for all of the PFAS that may be target compounds in this procedure as originally written or in the future, integration and quantitation of the PFAS is dependent on the type of isotopically labeled

standard and native compound materials available. Procedures in this section must be followed to identify and report the identity and quantity of PFAS found in source gas samples.

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 quantitative PFOA standard containing just 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 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, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures. Results must be reported individually for the filter, sorbent, impinger, 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 MDL 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.

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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:

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

Where,

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

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

$C_{is}$  = the concentration of the pre-extraction isotopically labeled analog in the standard (pg/ $\mu$ L).

$C_s$  = the concentration of the native compound in the continuing calibration standard (pg/ $\mu$ L).

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 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:

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

Where,

$A_n$  = The areas of the characteristic m/z for the target compound(s).

$A_i$  = The areas of the peak representing the primary m/z for the labeled compound.

$C_i$  = The concentration of the labeled compound in the calibration standard.

$C_n$  = The corresponding concentration of the native compound in the calibration standard.

12.6.2.3 Calculate the Concentration of Individual Target Compound in the Extract by Isotope Dilution (pg/ $\mu$ L). 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:

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

Where:

$C_{ex}$  = the concentration of the target compound in the extract in pg/ $\mu$ L.

$C_i$  = The concentration of the labeled compound in the calibration standard in pg/ $\mu$ L.

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$C_n$  = The concentration of the native compound in the calibration standard in pg/ $\mu$ L.

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.

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

Where,

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

$C_{ex}$  = The concentration of the compound in the extract in pg/ $\mu$ L.

$V_{ext}$  = The 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 where PFAS were detected.

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

Where,

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

12.6.3.1 In-stack Detectable Limit (DL). 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.]

$$DL = \frac{M_{MDLSum}}{dscm} \quad \text{Eq. 45-15}$$

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 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/ $\mu$ L) 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. Indicate whether reported masses 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 In-stacks DLs. For each run, report the sample-specific, in-stack DLs, based on run-specific QRL and MDL masses (sum of fractions 1-3) and the gaseous sample volume collected for that run.

### *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 45-9 and 45-10 present the pre-sampling standard recoveries and pre-extraction standard recoveries achieved as part of an ORD OTM-45 field evaluation. 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 are needed to better represent overall measurement performance. Candidates are limited to PFOA and PFOS at this time due to the lack of additional PFAS compounds with necessary multiple isotopologues. The pre-extraction standard recoveries presented in Table 45-10 also support OTM-45 performance criteria. In general, pre-extraction standard recoveries for Fractions 1 (Filter) and 3 (Impingers) were greater than for Fraction 2 (XAD-2).

Table 45-11 presents the calculated in-stack detection levels, based on both QRLs and MDLs and a nominal 3 m<sup>3</sup> 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<sup>3</sup> 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 to 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 interpret 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

- 1) EPA Method 533  
<https://www.epa.gov/sites/production/files/2019-12/documents/method-533-815b19020.pdf>
- 2) EPA Method 537.1  
[https://cfpub.epa.gov/si/si\\_public\\_record\\_Report.cfm?dirEntryId=343042&Lab=NERL](https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL)
- 3) EPA Method 5. 40 CFR Part 60 Appendix A-3
- 4) SW-846 Method 0010  
<https://www.epa.gov/hw-sw846/sw-846-test-method-0010-modified-method-5-sampling-train>.
- 5) Shoemaker, J. and Dan Tettenhorst. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Version 2.0, U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Solutions and Emergency Response, Cincinnati, OH, EPA Document #: EPA/600/R-20/006, 2020.
- 6) Rosenblum, L. and Wendelken, S. C. Method 533: Determination of Per- and Polyfluorinated Alkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water, Standards and Risk Management Division, Cincinnati, OH, EPA Document No. 815-B-19-020, 2019.
- 7) Tyner, T, and Francis, J. ACS reagent chemicals: specifications and procedures for reagents and standard-grade reference materials. American Chemical Society, <http://pubs.acs.org/isbn/9780841230460>, 2017.
- 8) U.S. Environmental Protection Agency. Office of Air Programs Publication No. APTD-0576: Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Research Triangle Park, NC. March 1972.
- 9) US EPA. *Statistical Protocol for the Determination of the Single-Laboratory Lowest Concentration Minimum Reporting Level (LCMRL) and Validation of Laboratory Performance at or Below the Minimum Reporting Level (MRL)*; EPA 815-R-05-006; Office of Water: Cincinnati, OH, November 2004.
- 10) US EPA. *Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator*; EPA 815-R-11-001; Office of Water: Cincinnati, OH, December 2010.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 45-1 PFAS Target Analytes

Common Name <sup>a</sup>	Abbreviated Name	CAS <sup>b</sup> Registry Number	Isotopic Pre-Extraction Pair
<b>Perfluoroalkylcarboxylic acids (PFCAs)</b>			
Perfluorobutanoic acid <sup>1,3,4</sup>	PFBA	375-22-4	<sup>13</sup> C <sub>4</sub> -PFBA
Perfluoropentanoic acid <sup>1,3,4</sup>	PFPeA	2706-90-3	<sup>13</sup> C <sub>5</sub> -PFPeA
Perfluorohexanoic acid <sup>1,2,3,4</sup>	PFHxA	307-24-4	<sup>13</sup> C <sub>2</sub> -PFHxA
Perfluoroheptanoic acid <sup>1,2,3,4</sup>	PFHpA	375-85-9	<sup>13</sup> C <sub>4</sub> -PFHpA
Perfluorooctanoic acid <sup>1,2,3,4</sup>	PFOA	335-67-1	<sup>13</sup> C <sub>4</sub> -PFOA
Perfluorononanoic acid <sup>1,2,3,4</sup>	PFNA	375-95-1	<sup>13</sup> C <sub>5</sub> -PFNA
Perfluorodecanoic acid <sup>1,2,3,4</sup>	PFDA	335-76-2	<sup>13</sup> C <sub>2</sub> -PFDA
Perfluoroundecanoic acid <sup>1,2,3,4</sup>	PFUnDA	2058-94-8	<sup>13</sup> C <sub>2</sub> -PFUnDA
Perfluorododecanoic acid <sup>1,2,3,4</sup>	PFDoA	307-55-1	<sup>13</sup> C <sub>2</sub> -PFDoA
Perfluorotridecanoic acid <sup>2,3,4</sup>	PFTTrDA	72629-94-8	<sup>13</sup> C <sub>2</sub> -PFDoA
Perfluorotetradecanoic acid <sup>2,3,4</sup>	PFTeDA	376-06-7	<sup>13</sup> C <sub>2</sub> -PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	<sup>13</sup> C <sub>2</sub> -PFHxDA
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	<sup>13</sup> C <sub>2</sub> -PFDoA
<b>Perfluorinated sulfonic acids (PFSAs)</b>			
Perfluoro-1-butanedisulfonic acid <sup>1,2,3,4</sup>	PFBS	375-73-5	<sup>13</sup> C <sub>3</sub> -PFBS
Perfluoro-1-pentadisulfonic acid <sup>1,3</sup>	PFPeS	2706-91-4	<sup>13</sup> C <sub>3</sub> -PFHxS Or <sup>13</sup> C <sub>3</sub> -PFBS
Perfluoro-1-hexadisulfonic acid <sup>1,2,3,4</sup>	PFHxS	355-46-4	<sup>18</sup> O <sub>2</sub> -PFHxS or <sup>13</sup> C <sub>3</sub> -PFHxS
Perfluoro-1-heptadisulfonic acid <sup>1,3</sup>	PFHpS	375-92-8	<sup>13</sup> C <sub>4</sub> -PFHpA
Perfluoro-1-octadisulfonic acid <sup>1,2,3,4</sup>	PFOS	1763-23-1	<sup>13</sup> C <sub>4</sub> -PFOS
Perfluoro-1-nonadisulfonic acid <sup>3</sup>	PFNS	68259-12-1	<sup>13</sup> C <sub>4</sub> -PFOS
Perfluoro-1-decadisulfonic acid <sup>3</sup>	PFDS	335-77-3	<sup>13</sup> C <sub>4</sub> -PFOS
Perfluorododecane sulfonate	PFDoS	79780-39-5	<sup>13</sup> C <sub>4</sub> -PFOS
<b>Perfluorinated sulfonamides (FOSAs)</b>			
Perfluoro-1-octanesulfonamide <sup>3,5</sup>	FOSA	754-91-6	<sup>13</sup> C <sub>8</sub> -FOSA
N-Methylperfluorooctanesulfonamide <sup>5</sup>	MeFOSA	31506-32-8	d3-MeFOSA
N-ethylperfluorooctanesulfonamide <sup>5</sup>	EtFOSA	4151-50-2	d5-EtFOSA
<b>Perfluorinated sulfonamide ethanols (FOSEs)</b>			
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol <sup>5</sup>	N-MeFOSE	24448-09-7	d7-N-MeFOSE
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol <sup>5</sup>	N-EtFOSE	1691-99-2	d9-N-EtFOSE
<b>Perfluorinated sulfonamidoacetic acids (FOSAAs)</b>			
N-methyl perfluorooctanesulfonamidoacetic acid <sup>2,3</sup>	MeFOSAA	2355-31-9	d3-MeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid <sup>2,3</sup>	EtFOSAA	2991-50-6	d5-EtFOSAA



<b>Fluorotelomer sulfonates (FTS)</b>			
1H,1H,2H,2H-Perfluorohexane sulfonic acid <sup>1,3</sup>	4:2 FTS	757124-72-4	M2-4:2 FTS
1H,1H,2H,2H -Perfluorooctane sulfonic acid <sup>1,3</sup>	6:2 FTS	27619-97-2	M2-6:2 FTS
1H,1H,2H,2H -Perfluorodecane sulfonic acid <sup>1,3</sup>	8:2 FTS	39108-34-4	M2-8:2 FTS
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0	M2-10:2 FTS
<b>Fluorinated Replacement Chemicals</b>			
4,8-Dioxa-3H-perfluorononanoic acid	ADONA <sup>1</sup>	919005-14-4	<sup>13</sup> C <sub>4</sub> -PFOS
Hexafluoropropylene Oxide Dimer Acid	HFPO-DA (GenX) <sup>1</sup>	13252-13-6	<sup>13</sup> C <sub>3</sub> -HFPO-DA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS (F-53B Major) <sup>1</sup>	756426-58-1	<sup>13</sup> C <sub>4</sub> -PFOS
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid OR 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate <sup>a</sup>	11Cl-PF3OUdS (F-53B Minor) <sup>1</sup>	763051-92-9 83329-89-9	<sup>13</sup> C <sub>4</sub> -PFOS
<b>Additional Targets</b>			
Nonafluoro-3,6-dioxaheptanoic acid <sup>1,5</sup>	NFDHA	151772-58-6	<sup>13</sup> C <sub>5</sub> -PFHxA
Perfluoro(2-ethoxyethane)sulfonic acid <sup>1,5</sup>	PFEESA	113507-82-7	<sup>13</sup> C <sub>3</sub> -PFBS
Sodium perfluoro-1-dodecanesulfonate <sup>5</sup>	PFDoS	1260224-54-1	<sup>13</sup> C <sub>4</sub> -PFOS
Perfluoro-4-methoxybutanoic acid <sup>1,5</sup>	PFMBA	863090-89-5	<sup>13</sup> C <sub>5</sub> -PFPeA
Perfluoro-3-methoxypropanoic acid <sup>1,5</sup>	PFMPA	377-73-1	<sup>13</sup> C <sub>4</sub> -PFBA
Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate <sup>4</sup>	PFecHS	67584-42-3	<sup>18</sup> O <sub>2</sub> -PFHxS
2H-perfluoro-2-decenoic acid <sup>4</sup>	8:2 FTUCA or FOUEA	70887-84-2	<sup>13</sup> C <sub>2</sub> -FOUEA
2-perfluorodecyl ethanoic acid <sup>4</sup>	10:2 FDEA	53826-13-4	<sup>13</sup> C <sub>2</sub> -FDEA
2-perfluorooctyl ethanoic acid <sup>4</sup>	8:2 FTA or FOEA	27854-31-5	<sup>13</sup> C <sub>2</sub> -FOEA
2H-perfluoro-2-octenoic acid <sup>4</sup>	6:2 FHUEA	70887-88-6	<sup>13</sup> C <sub>2</sub> -FHUEA
2-perfluorohexyl ethanoic acid <sup>4</sup>	6:2FTCA or 6:2 FHEA	53826-12-3	<sup>13</sup> C <sub>2</sub> -FHEA
3:3 Fluorotelomer carboxylic acid <sup>5</sup>	3:3 FTCA	356-02-5	<sup>13</sup> C <sub>2</sub> -FHEA
5:3 Fluorotelomer carboxylic acid <sup>5</sup>	5:3 FTCA	914637-49-3	<sup>13</sup> C <sub>2</sub> -FHEA
7:3 Fluorotelomer carboxylic acid or 3-perfluoropheptyl propanoic acid <sup>4,5</sup>	7:3 FTCA or FHpPA	812-70-4	<sup>13</sup> C <sub>2</sub> -FOEA

<sup>a</sup> 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

<sup>b</sup> Chemical Abstract Service.

<sup>1</sup> Compound targeted in EPA Method 533

<sup>2</sup> Compound targeted in EPA Method 537.1

<sup>3</sup> Compound targeted in EPA Method 8327

<sup>4</sup> Compound targeted in ASTM Method D7968

<sup>5</sup> Compound targeted in DoD Isotope Dilution Method

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	
<sup>13</sup> C <sub>3</sub> -PFBA	216	172	
<sup>13</sup> C <sub>4</sub> -PFBA	217	172	
PFPeA	263	219	
<sup>13</sup> C <sub>5</sub> -PFPeA	268	223	
PFH <sub>x</sub> A	313	269	119
<sup>13</sup> C <sub>5</sub> -PFH <sub>x</sub> A	318	273	
PFHpA	363	319	169
<sup>13</sup> C <sub>4</sub> -PFHpA	367	322	
PFOA	413	369	169
<sup>13</sup> C <sub>2</sub> -PFOA	415	370	
<sup>13</sup> C <sub>8</sub> -PFOA	421	376	
PFNA	463	419	169
<sup>13</sup> C <sub>9</sub> -PFNA	472	427	
PFDA	513	469	169
<sup>13</sup> C <sub>6</sub> -PFDA	519	474	
PFUnA	563	519	169
<sup>13</sup> C <sub>7</sub> -PFUnA	570	525	
PFDoA	613	569	169
<sup>13</sup> C <sub>2</sub> -PFDoA	615	570	
PFT <sub>r</sub> DA	663	619	169
PFTeDA	713	169	219
PFH <sub>x</sub> DA	813	769	169
PFODA	913	869	169
PFBS	299	80	99
<sup>13</sup> C <sub>3</sub> -PFBS	302	80	83
PFPeS	349	80	99
PFH <sub>x</sub> S	399	80	99
<sup>13</sup> C <sub>3</sub> -PFH <sub>x</sub> S	402	80	
PFHpS	449	80	99
PFOS	499	80	99
<sup>13</sup> C <sub>4</sub> -PFOS	503	80	
<sup>13</sup> C <sub>8</sub> -PFOS	507	80	
PFNS	549	80	99
PFDS	599	80	99
PFDoS	699	80	99
FOSA	498	78	
MeFOSA	512	169	
EtFOSA	526	169	
N-MeFOSE	616	59	
N-EtFOSE	630	59	
MeFOSAA	570	419	512
EtFOSAA	584	419	526
4:2FTS	327	307	

<sup>13</sup> C <sub>2</sub> -4:2FTS	329	309	81
6:2FTS	427	407	
<sup>13</sup> C <sub>2</sub> -6:2FTS	429	409	81
8:2FTS	527	507	
<sup>13</sup> C <sub>2</sub> -8:2FTS	529	509	81
10:2FTS	627	607	80
ADONA	377	251	
HFPO-DA	285	169	
<sup>13</sup> C <sub>3</sub> -HFPO-DA	287	169	
9Cl-PF3ONS	531	351	
11Cl-PF3OUdS	631	451	
NFDHA	295	201	
PFEESA	315	135	
PFDoS	699	80	99
PFMBA	279	85	
PFMPA	229	85	
PFecHS	461	381	99
8:2 FTUCA or FOUEA	457	393	
10:2 FDEA	577	493	
8:2 FTA or FOEA	477	393	
6:2 FHUEA	357	293	
6:2FTCA or 6:2 FHEA	377	243	
3:3 FTCA	241	177	117
5:3 FTCA	341	237	217
7:3 FTCA or FHpPA	441	337	317

Table 45-3 Fortification and Recovery Solutions for Poly and Perfluorinated Alkyl Compounds<sup>a</sup>

Compound	Amount ( $\mu\text{g}/\mu\text{L}$ of final extract) <sup>b</sup>	Spike Recovery (percent)
<b>Pre-sampling Adsorbent Standards</b>		
<sup>13</sup> C <sub>8</sub> PFOA	75	70-130
<sup>13</sup> C <sub>8</sub> PFOS	75	70-130
<b>Pre-extraction Filter Recovery Spike Standards</b>		
<b>Needs to be identified</b>	<b>75</b>	<b>70-130</b>
<b>Pre-extraction Standards</b>		
	50	20-130
<sup>13</sup> C <sub>4</sub> PFBA	50	20-130
<sup>13</sup> C <sub>5</sub> PFPeA	50	20-130
<sup>13</sup> C <sub>2</sub> PFHxA	50	20-130
<sup>13</sup> C <sub>4</sub> PFHpA	50	20-130
<sup>13</sup> C <sub>4</sub> PFOA	50	20-130
<sup>13</sup> C <sub>5</sub> PFNA	50	20-130
<sup>13</sup> C <sub>2</sub> PFDA	50	20-130
<sup>13</sup> C <sub>2</sub> PFUnA	50	20-130
<sup>13</sup> C <sub>2</sub> PFDoA	50	20-130
<sup>13</sup> C <sub>2</sub> PFTeDA	50	20-130
<sup>13</sup> C <sub>2</sub> -PFHxDA	50	20-130
<sup>13</sup> C <sub>2</sub> -PFDoA	50	20-130
<sup>13</sup> C <sub>3</sub> - PFBS	50	20-130
<sup>13</sup> C <sub>3</sub> -PFHxS	50	20-130
<sup>18</sup> O <sub>2</sub> PFHxS	50	20-130
<sup>13</sup> C <sub>4</sub> PFOS	50	20-130
<sup>13</sup> C <sub>8</sub> FOSA	50	20-130
d <sub>3</sub> -NMeFOSAA	50	20-130
d <sub>5</sub> -NEtFOSAA	50	20-130
d <sub>7</sub> -N-MeFOSE	50	20-130
d <sub>9</sub> -N-EtFOSE	50	20-130
M2-6:2 FTS	50	20-130
M2-8:2 FTS	50	20-130
M2-4:2 FTS	50	20-130
M2-10:2 FTS (D4 labeled)	50	20-130
<sup>13</sup> C <sub>3</sub> HFPO-DA	50	20-130
<sup>13</sup> C <sub>2</sub> -FOUEA	50	20-130
<sup>13</sup> C <sub>2</sub> -FDEA	50	20-130
<sup>13</sup> C <sub>2</sub> -FOEA	50	20-130
<sup>13</sup> C <sub>2</sub> -FHUEA	50	20-130
<sup>13</sup> C <sub>2</sub> -FHEA	50	20-130
<b>Pre-analysis Standards</b>		
<sup>13</sup> C <sub>2</sub> PFOA	50	S/N $\geq$ 10
<sup>13</sup> C <sub>3</sub> -PFBA	50	S/N $\geq$ 10

<sup>a</sup> 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. Spike concentration assumes 1 $\mu\text{L}$  sample injection volume for analysis.

<sup>b</sup> Spike levels assume half of the extract will be archived before cleanup. Spike levels may be adjusted for different split levels.

**Table 45- 4 Sample Storage Conditions<sup>a</sup> and Laboratory Hold Times**

Stage	Type	Storage Conditions	Laboratory Holding time
Field collection	Particulate Filter	$\leq 20 \pm 3$ °C, $68 \pm 5$ °F Store cool but NOT on ice	N/A
	All other Field samples	Store on Ice (4°C)	
Shipping/Transport	Particulate Filter	Ship unrefrigerated.	N/A
	All other Field samples	Ship on Ice (4°C). Follow procedures in ASTM D6911-15	
Laboratory Storage: Before Extraction	All Sampling train Rinses and Particulate Filter Samples	$\leq 6$ °C (43°F)	$\leq 28$ days from date of collection; Extract within 28 days of collection
	Adsorbent samples (XAD-2)	$\leq 6$ °C (43°F)	$\leq 1$ year from received date; Extract within 28 days of collection
Laboratory Storage: After Extraction (archived)	All archived extracted samples	at $\leq 6$ °C (43°F)	$\leq 1$ year

<sup>a</sup> 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
<b>Sampling Quality Controls (Section 9.1)</b>				
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 $\leq$ 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 $\leq$ 10% of actual samples	If $>$ 10%, flag data and assess impact on results
9.1.4	Sample Train Field Blank (STFB)	At least one STPB per each test series	Levels $\leq$ 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.	$\geq$ 70% and $\leq$ 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 Breakthrough	Determines the relative breakthrough (BT) of each target through the OTM-45 train.	≤30% BT for each target compound.	For any BT ≥ 10%, add the fraction 4 mass to the total sample mass for emissions calculations If >30%, flag data and assess impact on results. Failure may invalidate reported results and require repeat sampling.
<b>Ongoing Quality Control Requirements (Section 9.2.2)</b>				
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 <b>and</b> ≥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 ≤ MDL 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 in the initial calibration.	If criteria is 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 samples extract.
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 should 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.
9.2.2.78	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 Laboratory Sample media Blank (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 MDL's 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 $\leq$ 150% Lower PIR $\geq$ 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 Laboratory Fortified Media Blanks (LFMBs) near the mid-range concentration.	Percent relative standard deviation must be $\leq$ 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 $\leq$ 150% Lower PIR $\geq$ 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/uL)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
<b>Perfluoroalkylcarboxylic acids (PFCAs)</b>							
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
PFTTrDA	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
<b>Perfluorinated sulfonic acids (PFSAs)</b>							
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
<b>Perfluorinated sulfonamides (FOSAs)</b>							
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
<b>Perfluorinated sulfonamide ethanols (FOSEs)</b>							
MeFOSE	0.25	0.50	1	2.5	5	20	100
EtFOSE	0.25	0.50	1	2.5	5	20	100
<b>Perfluorinated sulfonamidoacetic acids (FOSAAs)</b>							
EtFOSAA	0.25	0.50	1	2.5	5	20	100
MeFOSAA	0.25	0.50	1	2.5	5	20	100
<b>Fluorotelomer sulfonates (FTS)</b>							
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
<b>Fluorinated Replacement Chemicals</b>							
ADONA <sup>1</sup>	0.25	0.50	1	2.5	5	20	100
HFPO-DA (GenX) <sup>1</sup>	0.25	0.50	1	2.5	5	20	100
<sup>9</sup> Cl-PF <sub>3</sub> ONS (F-53B Major) <sup>1</sup>	0.25	0.50	1	2.5	5	20	100
F-53B Minor ( <sup>11</sup> Cl-PF <sub>3</sub> OUdS) <sup>1</sup>	0.25	0.50	1	2.5	5	20	100
F5B minor ( <sup>11</sup> Cl-PF <sub>3</sub> OUdS)	0.25	0.50	1	2.5	5	20	100
<b>Additional Targets</b>							
NFDHA	0.25	0.50	1	2.5	5	20	100
PFEESA	0.25	0.50	1	2.5	5	20	100
PFDoS	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
<i>PFecHS</i>	0.25	0.50	1	2.5	5	20	100
8:2 FTUCA or FOUEA	0.25	0.50	1	2.5	5	20	100
10:2 FDEA	0.25	0.50	1	2.5	5	20	100
8:2 FTA or FOEA	0.25	0.50	1	2.5	5	20	100
6:2 FHUEA	0.25	0.50	1	2.5	5	20	100
6:2 FTCA or 6:2 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 Or FHpPA	0.25	0.50	1	2.5	5	20	100

Table 45-8 Isotopic Dilution Pairs Initial Calibration (ICAL) Concentration (pg/uL)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
<b>Perfluoroalkylcarboxylic acids (PFCAs)</b>							
<sup>13</sup> C <sub>4</sub> -PFBA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>5</sub> -PFPeA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -PFHxA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFHpA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>5</sub> -PFNA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -PFDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -PFUDa	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -PFDoA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -PFTeDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Perfluorinated sulfonic acids (PFSAs)</b>							
<sup>13</sup> C <sub>3</sub> - PFBS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>3</sub> -PFHxS (533) Or <sup>13</sup> C <sub>3</sub> -PFBS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>18</sup> O <sub>2</sub> -PFHxS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFHpA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Perfluorinated sulfonamides (FOSAs)</b>							
<sup>13</sup> C <sub>8</sub> -FOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d5-EtFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d3-MeFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Perfluorinated sulfonamide ethanols (FOSEs)</b>							
d7-N-MeFOSE	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d9-N-EtFOSE	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Perfluorinated sulfonamidoacetic acids (FOSAAs)</b>							
d5-EtFOSAA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d3-MeFOSAA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Fluorotelomer sulfonates (FTS)</b>							
M2-4:2 FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
M2-6:2 FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
M2-8:2 FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Fluorinated Replacement Chemicals</b>							
<sup>13</sup> C <sub>4</sub> -PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>3</sub> -HFPO-DA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<b>Pre-analysis Spiking Standard</b>							
<sup>13</sup> C <sub>2</sub> -PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 45-8 Continued Isotopic Dilution Pairs Initial Calibration (ICAL) Concentration (pg/uL)

<sup>13</sup> C <sub>5</sub> -PFHxA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>3</sub> -PFBS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>5</sub> -PFPeA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>4</sub> -PFBA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -FOUEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -FDEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -FOEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -FHUEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
<sup>13</sup> C <sub>2</sub> -FHEA	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 45-9 Pre-Sampling Standard Recoveries

Pre-Sampling Standard	Percent (%) Recovery			
	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 45-10 Pre-Extraction Standard Recoveries

Pre-Extraction Standard	Fraction 1 (Filter) Percent (%) Recovery				Fraction 2 (XAD-2) Percent (%) Recovery				Fraction 3 (Impingers) Percent (%) Recovery			
	Avg	RSD	Max	Min	Avg	RSD	Max	Min	Avg	RSD	Max	Min
13C2 PFDA	98	6.8%	107	92	72	16.9%	83	55	112	8.2%	124	102
13C2 PFDoA	98	5.3%	102	90	84	25.7%	105	54	114	12.6%	132	98
13C2 PFHxA	98	7.1%	108	92	85	7.0%	93	80	106	7.4%	115	97
13C2 PFTeDA	93	9.9%	104	82	75	31.8%	107	50	113	12.2%	127	94
13C2 PFUnA	101	7.9%	110	91	80	21.4%	94	55	112	9.7%	126	100
13C3 HFPO-DA	79	6.3%	84	74	72	12.0%	79	60	104	11.3%	121	96
13C4 PFBA	94	6.7%	103	89	56	12.5%	65	49	102	8.4%	114	94
13C4 PFHpA	100	4.8%	106	95	76	5.6%	81	71	111	9.4%	124	99
13C4 PFOA	99	6.9%	108	92	88	10.3%	99	78	108	10.0%	120	94
13C4 PFOS	92	4.7%	98	89	82	19.2%	94	59	108	9.1%	120	96
13C5 PFNA	99	6.1%	106	92	81	14.5%	93	65	114	10.0%	128	100
13C5 PFPeA	93	6.9%	101	86	64	6.5%	68	60	101	7.5%	111	93
13C8 FOSA	89	8.7%	99	80	55	48.0%	89	25	108	8.1%	120	99
18O2 PFHxS	105	4.1%	111	101	81	9.8%	86	69	119	10.4%	135	105
d3-NMeFOSAA	83	13.1%	93	68	77	25.7%	100	52	94	9.4%	106	85
d5-NEtFOSAA	104	8.2%	111	93	84	28.6%	108	51	97	16.1%	118	82
M2-4:2 FTS	110	13.8%	129	92	156	11.8%	174	131	110	21.1%	131	80
M2-6:2 FTS	118	18.8%	144	91	143	25.6%	186	97	130	28.4%	176	86
M2-8:2 FTS	121	29.3%	167	82	89	25.0%	105	57	113	17.5%	135	87

**Table 45-11. In-Stack Detection Limits**

<b>Analyte Description</b>	<b>CAS Number</b>	<b>QRL (ng/train)</b>	<b>MDL (ng/train)</b>	<b>QRL (ng/m3)</b>	<b>MDL (ng/m3)</b>	<b>QRL (PPQ)</b>	<b>MDL (PPQ)</b>
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



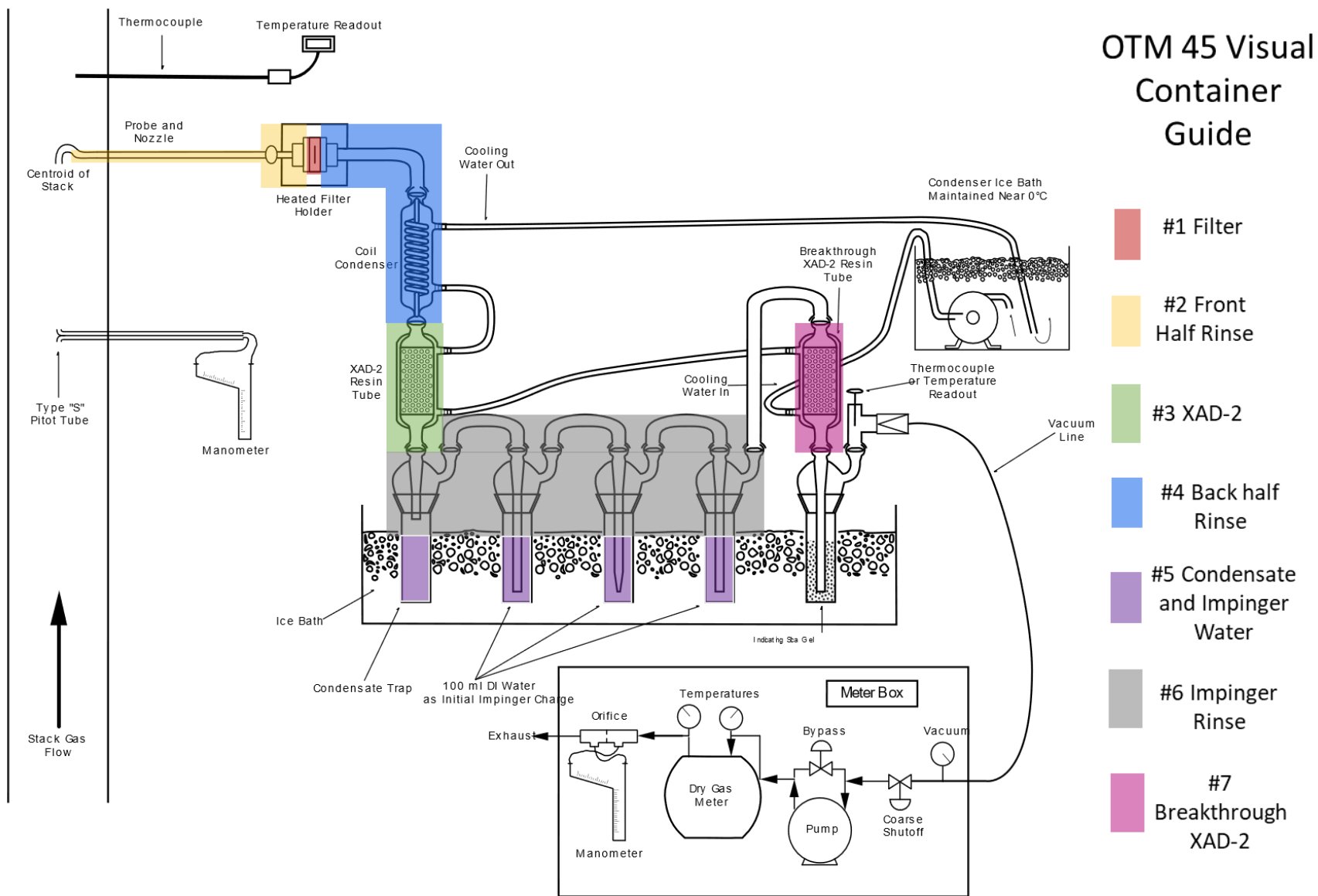


Figure OTM-45-1. Sampling Train

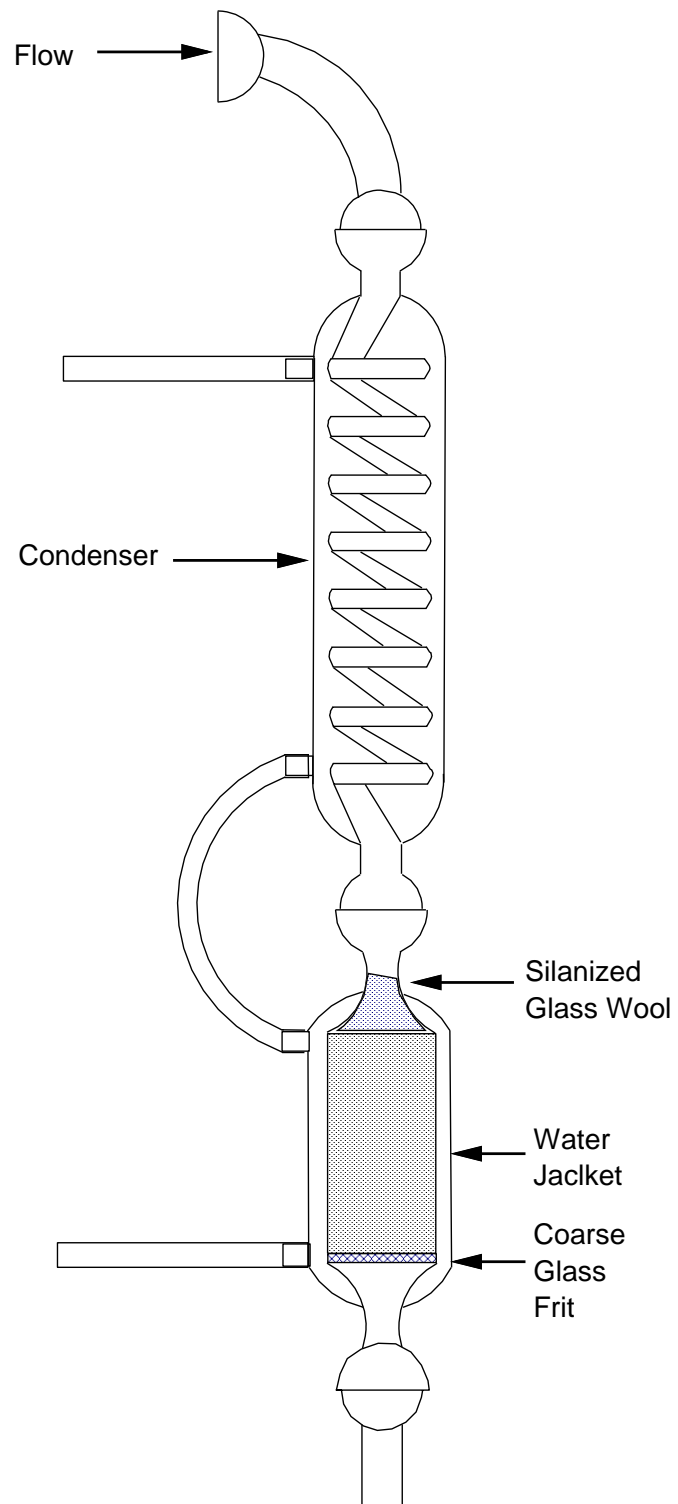


Figure OTM 45-2. Condenser and Adsorbent Module

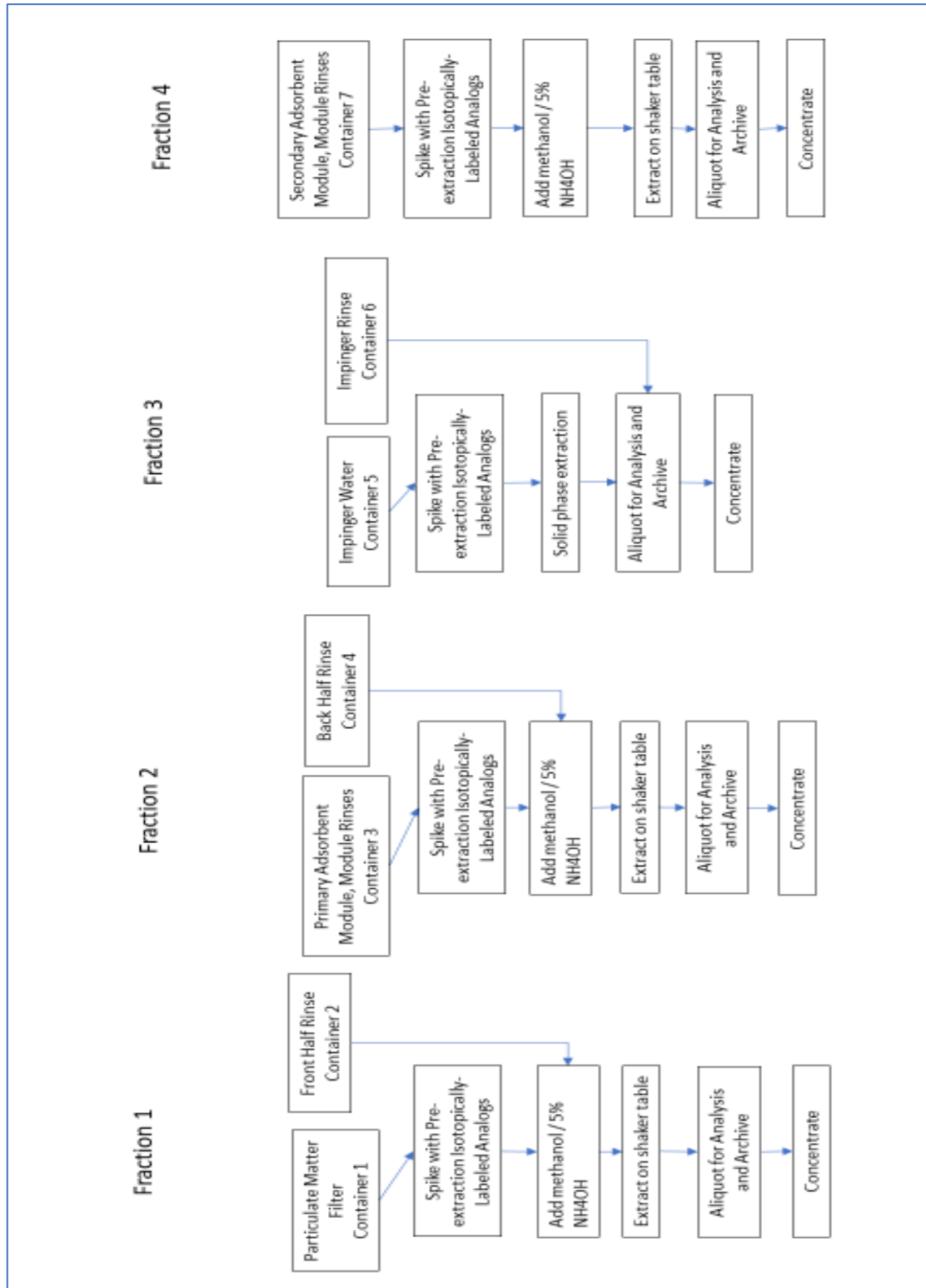


Figure OTM 45-3. Sample Preparation Flow Chart

## 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 13.14 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 hr.
- Methyl alcohol: Extract for 22 hr.
- Methylene chloride: Extract for 22 hr.
- 5% ammonium hydroxide in methanol: Extract for 22 hr.

Note: You may store the resin in a sealed glass container filled with 5% 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 liter of distilled water for every 25 g

of resin. A small pump may be useful for pumping the water through the canister. You should 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.

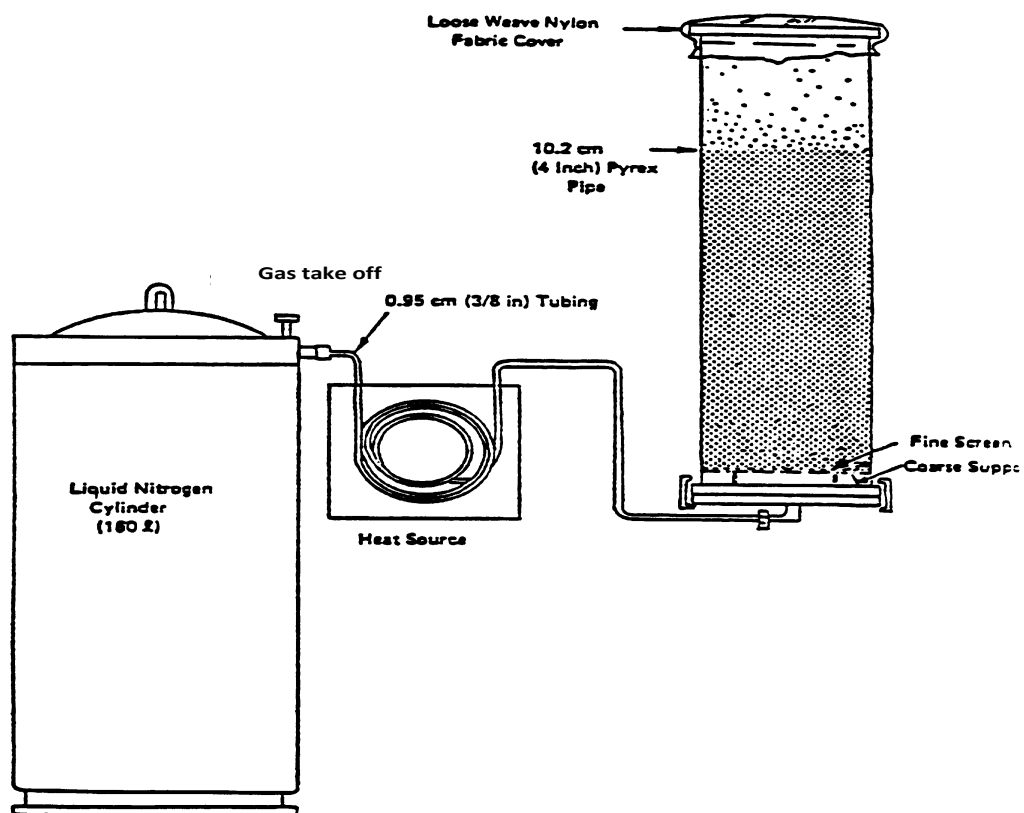


Figure A-1. XAD-2 fluidized-bed drying apparatus