Title: Extraction of 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (HFPO-DA) in Method 0010 Sampling Trains and Surface Wipe Samples

Approvals (Signature/Date):

David L. Wiles	7/31/18 Date	Lewis Osborne	7-31-18 Date
Technical Manager		Health & Safety Manager / Coordinator	
Kevin McGee	7/31/18 Date	Christopher Rigell	08/07/18 Date
Quality Assurance Manager		Laboratory Director	

Facility Distribution No. NA **Distributed To:** UNC

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedure to be used for the extraction of HFPO-DA (CAS # 13252-13-6) from Method 0010 Sampling Train matrices, including filters & associated rinses ("front-half"), XAD®-2 resin tubes & associated rinses ("back-half"), impinger condensate composites (water), and from surface wipe samples.

1.2 This procedure does not describe the LC/MS/MS instrumental analysis of the extracts. For those details, see DV-LC-0012 "Analysis of Perfluorooctanoic Acid (PFOA) and other Perfluorinated Hydrocarbons (PFCs) and Perfluorinated Hydrocarbon Sulfonates (PFSs) in Water and Soil by LC/MS/MS".

1.3 Reporting limits will vary depending on sample volumes and dilution factors. See Table 1 for reporting limits that are based on an assigned standard extract volume of each Method 0010 or Surface Wipe matrix.

2.0 SUMMARY OF METHOD

2.1 Front-Half Composites (particulate filter, probe, nozzle, and filter housing solvent rinses) are extracted with methanol / 5% ammonium hydroxide (CH_3OH / 5% NH_4OH) on a shaker table for 18 hours (minimum), filtered, and brought to a 1:1 volume with DI water / 5% ammonium hydroxide, then HFPO-DA is reformulated with 2% formic acid. A portion of the final extract is filtered through a polyethylene disk filter for analysis.

2.2 Back-Half Composites (XAD®-2 resin tubes and back-half glassware solvent rinses) are extracted with methanol / 5% ammonium hydroxide (CH_3OH / 5% NH_4OH) on a shaker table for 18 hours (minimum), the extraction solvent is decanted and the sample is extracted a second time with fresh solvent for another 18 hours (minimum). The extracts are combined and brought to a 1:1 volume with DI water / 5% ammonium hydroxide, then HFPO-DA is reformulated with 2% formic acid. A portion of the final extract is filtered through a polyethylene disk filter for analysis.

2.3 Wipe samples are extracted with methanol / 5% ammonium hydroxide (CH_3OH / 5% NH_4OH) on a shaker table for 18 hours (minimum), filtered, and brought to a 1:1 volume with DI water / 5% ammonium hydroxide, then HFPO-DA is reformulated with 2% formic acid. A portion of the final extract is filtered through a polyethylene disk filter for analysis.

2.4 The volume of the Impinger Condensate Composite (water) samples are measured and $1/20^{th}$ of the sample is brought to 250 mL in DI water to send to Denver for analysis.

2.5 $^{13}C_3$ HFPO-DA is used in this analysis as an isotope dilution internal standard (IDA). The isotope dilution technique corrects the final analytical results for analytical recovery losses encountered when analyzing more chemically complex environmental samples. A known quantity of the labeled PFC compounds (IDA) is added to every sample and to the batch quality control samples prior to extraction. Because the isotopically labeled compound is chemically equivalent to the target compound being evaluated, it is affected by interfering substances or target

compound recovery losses from the samples to the same extent as the target compound. The recovery of the labeled PFC's is then used to mathematically correct the final concentration results for the PFC's.

3.0 DEFINITIONS

Refer to the Laboratory's Quality Assurance Manual (QAM) for the Glossary of Terms, Definitions and Acronyms except as follows:

3.1 HFPO-DA: 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid (CAS # 13252-13-6)

3.2 IDA: Isotope-dilution internal analyte or standard

3.3 XAD®-2 resin: A porous polymeric adsorbent resin typically used for semivolatile compound air sampling.

4.0 INTERFERENCES

4.1 Care should be taken not to cross-contaminate samples during the preparation/extraction stages. An extreme range of concentrations are likely to be encountered during sample handling, and appropriate sample handling, Isolation, and storage planning should be undertaken.

4.2 Approved solvents are demonstrated to be free from interferences by analysis of laboratory method blanks.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

5.4 Specific Safety Concerns or Requirements

5.4.1 Eye protection that satisfies ANSI Z87.1 (as per the Environmental Health and Safety Manual), laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4.2 Methanol is flammable and used throughout this procedure. Methanol should be stored away from any ignition sources and kept in closed containers with secondary containment measures or within a fume hood.

5.5 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Methanol (MeOH)	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Ammonium hydroxide	Corrosive Toxic	25 ppm (TWA)	Causes severe burns and possible irreversible eye damage. May cause severe and permanent damage to the digestive tract.
Formic acid	Combustible Corrosive Flammable Toxic	5 ppm (TWA)	Causes severe burns, toxic by inhalation, harmful if swallowed, possible sensitizer.
1 - Always add acid to water to prevent violent reactions. 2 - Exposure limit refers to the OSHA regulatory exposure limit.			

5.6 Waste Management and Pollution Prevention

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

6.0 EQUIPMENT AND SUPPLIES

6.1 Equipment

6.1.1 Shaker table apparatus for sample extractions

6.1.2 Volumetric Flasks (Class A): 100 mL

6.1.3 Graduated cylinder: 100 mL, 1000 mL

6.1.4 Hamilton glass syringe, 1 mL

6.2 Supplies

6.2.1 Glass disposable pipettes: 10 mL, 5 mL, 2 mL

6.2.2 Nalgene® containers: 1000 mL, 500 mL, 250 mL, 125 mL

6.2.3 Glass Fiber Particulate Filter: Glass fiber filters, without organic binder, exhibiting at least 99.95% efficiency (< 0.05% penetration) on 0.3 µm dioctyl phthalate smoke particles. Whatman 934-AH glass fiber filters are the TestAmerica stock item used.

6.2.4 XAD®-2 Sorbent resin - Amberlite® XAD®-2 resin or equivalent (Supelco Supelpak 2-SVM)

6.2.5 Disposable plastic syringe, 10-mL

6.2.6 Syringe filter, 0.45 µm

6.2.7 Disposable plastic funnel

6.2.8 Metal funnel

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water is produced by a Millipore DI system or equivalent. Reagent water must be free of the analyte of interest as demonstrated through the analysis of appropriate method blanks.

7.1.2 Methanol (MeOH,) HPLC grade or equivalent

7.1.3 Ammonium hydroxide (NH_4OH), ACS grade or equivalent

7.1.4 Formic acid, Reagent grade or equivalent

7.1.5 Extraction solvent: MeOH / 5% NH_4OH:

50 mL NH_4OH is brought to 1000 mL with MeOH

7.1.6 Diluent: Reagent water / 5% NH_4OH:

50 mL NH_4OH is brought to 1000 mL with DI water

7.1.7 2% Formic acid solution:

20 mL formic acid is brought to 1000 mL with DI water.

7.2 Stock Standard Materials

7.2.1 $^{13}C_3$ HFPO-DA - Wellington, Catalog # - M3HFPO-DA, 50 µg/mL in MeOH

7.2.2 HFPO-DA - Wellington, Catalog # - HFPO-DA, 50 µg/mL in MeOH

7.2.3 The stock standard solutions are stored at ≤6°C. Stock standard solutions should be brought to room temperature before using. Standards are monitored for signs of degradation or evaporation. Standard solutions must be replaced at least annually from the date of opening or earlier if the vendor indicates an earlier expiration date

7.3 Spiking Solutions (LCS & IDA)

7.3.1 All spiking solutions are stored in Nalgene® containers at ≤6°C and are assigned an expiration date of one year or earlier if the parent stock materials have an earlier expiration date. Dilutions from stocks may not be assigned expiration dates that exceed the expiration of the stock materials.

7.3.2 The LCS & IDA spiking solutions are prepared by diluting the appropriate amounts of stock solutions in HPLC-grade methanol to a concentration of 0.5 µg/mL. The LCS spiking solution is also used to spike the MS and MSD samples.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sampling containers, preservation techniques and sample holding times are dependent on the specific sample matrix, analytical method of choice, regulatory compliance requirements, and/or specific contract or client requirements. Listed below are the assigned sample holding times and preservation requirements.

Matrix	Sample Container	Preservation	Extraction Holding Time
Impinger Condensate (Waters)	Nalgene®	Cool ≤ 6°C	14 Days
Particulate Filters	Nalgene®	Cool ≤ 6°C	14 Days
XAD®-2	Sampling cartridge	Cool ≤ 6°C	14 Days
Surface Wipes	Nalgene®	Cool ≤ 6°C	14 Days

9.0 QUALITY CONTROL

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section.

9.1.1 Project-specific requirements can override the general requirements presented in this section when there is a written agreement between the analytical laboratory and the client (or client's agent), and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method or Sample Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders

9.1.2 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP KNOX-QA-0008. This is in addition to the corrective actions described in the following sections

9.2 Initial Performance Studies

The laboratory must establish a method detection limit (MDL) for each matrix. In addition, an initial demonstration of capability (IDOC) must be performed by each analyst for each matrix. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence.

9.4 Method Blank (MB)

One method blank must be processed with each preparation batch of 10 field samples. The method blank is processed and analyzed just as if it were a sample.

9.4.1 The method blank for batches of aqueous samples consists of 250 mL of Reagent DI water.

9.4.2 The method blank for batches of media samples (XAD®-2 resin, particulate filter, surface wipe gauze pads) consists of the same matrix as used for collection.

9.5 Laboratory Control Sample (LCS)

At least one LCS must be processed with each preparation batch. The LCS is carried through the entire analytical procedure just as if it were a sample.

9.5.1 For aqueous sample batches, the LCS consists of 250 mL of Reagent DI water.

9.5.2 For media collection samples (XAD®-2 resin, particulate filters, surface wipes), the LCS consists of the same matrix as used for sample collection.

9.6 Isotopically Labeled Internal Standard (IDA)

Every field sample and QC sample (i.e. method blank, LCS, MS, and MSD) is spiked with the isotope dilution internal standard compounds.

9.7 Summary of batch requirements

QC Sample	***Frequency***	***Control Limit***
Method Blank (MB)	1 per batch (batch = 1 to 20 samples)	≤ RL
Lab Control Sample (LCS)[2]	1 per batch	50 – 150%; 35% RPD
Matrix Spike (MS)[1,3,5]	1 per batch, if applicable	50 – 150%
MS Duplicate (MSD) [1,3,5]	1 per batch, if applicable	50 – 150%; 35% RPD
IDA	Applied to each analytical & QC sample	50-200%[6]

[1] Limits only apply if the sample concentration is ≤4X spike level; if sample concentration is >4X spike level, limits do not apply and the data is flagged.

[2] An LCS Duplicate (LCSD) is performed only when requested by the client/project/contract.

[3] The sample selection for MS/MSD is randomly selected, unless specifically requested by a client.

[4] Statistical control limits are updated annually.

[5] An MS/MSD set of analyses cannot be performed on an XAD®-2 resin material or particulate filter sample.

[6] Only applies to dilutions of up to 50x.

10.0 SAMPLE PREPARATION PROCEDURE

10.1 Front-half Composites (particulate filter and probe, nozzle, filter housing solvent rinses)

10.1.1 Align all front-half particulate filters sample fractions with their appropriate solvent rinses on a counter. Solvent rinses are composed of methanol / 5% ammonium hydroxide.

10.1.2 Measure the volumes of the solvent rinses received for each of the samples in order to determine the appropriate amounts of IDA spiking materials to

be added to the samples, in addition to the amounts of other reagents to be used in the sample preparations. These measured volumes are also used to determine the final volumes that the samples to be brought to upon completion of the prep. See Table 2 for the proportions of reagents that relate to the glassware solvent rinses received from the field.

10.1.3 The nominal final volume for a front-half sample is 50 mL made up by the following reagents:

- 1 mL of 0.5 µg/mL IDA
- 22 mL of methanol / 5% ammonium hydroxide (includes field solvent rinse volume)
- 22 mL of reagent water / 5% ammonium hydroxide
- 5 mL of 2% formic acid

10.1.4 The particulate filters are placed into an appropriate Nalgene container for preparation.

10.1.5 The particulate filters are initially spiked with the appropriate amount of IDA and the front-half solvent rinses are then added to the sample. Additional extraction solvent (methanol / 5% ammonium hydroxide) is added to the sample in order to bring the volume of methanol / ammonium hydroxide in the prep container up to the appropriate volume (in 22 mL increments). For example, if a solvent rinse volume is 30 mL as received, then the final total amount of extraction solvent with the rinse is 44 mL. Therefore, 2 mL of IDA and 14 mL of methanol / 5% ammonium hydroxide extraction solvent should be added to the sample and rinse in this example.

10.1.6 A particulate filter method blank and a particulate filter LCS are required for this Method 0010 sample fraction preparation. Note that an additional 1 mL portion of a 0.5 µg/mL HFPO-DA native spike is added to the LCS prior to the addition of extraction solvent.

10.1.7 Samples are extracted on a shaker table for a minimum of 18 hours.

10.1.8 After extraction of the front-half composite samples is completed, the extraction solvent is filtered into a separate appropriately sized Nalgene container by placing a filter paper in disposable plastic funnels and pouring the sample extracts through the funnels and into the Nalgene containers.

10.1.9 Enough reagent water / 5% ammonium hydroxide is then added to the sample to bring it to a 1:1 ratio with the original extraction solvent (i.e. 22 mL methanol / 5% ammonium hydroxide: 22 mL reagent water / 5% ammonium hydroxide).

10.1.10 A 2% formic acid solution is then added to each sample to achieve a ratio of 5 mL 2% formic acid for each 22 mL of methanol / 5% ammonium hydroxide extraction solvent. Each sample is then mixed thoroughly.

10.1.11 Approximately 5-6 mL of each front-half sample extract is filtered through a 0.45 µm polyethylene disk using a disposable, plastic syringe. The remainder of the sample extract portions is archived in an appropriate refrigerator.

10.2 Back-half Composite (XAD®-2 resin and back-half glassware solvent rinses)

10.2.1 Align and organize all back-half (XAD®-2) sample fractions with their attendant solvent rinses on a counter. Solvent rinses are composed of methanol / 5% ammonium hydroxide (CH_3OH / 5% NH_4OH).

10.2.2 Measure and record the individual volumes of the rinses for each of the samples in order to determine the appropriate IDA spike volumes to add to the samples, in addition to the volumes of the other reagents used to prepare the final sample extracts. The measured volumes are also used to determine the final extract volumes for these samples. See Table 2 for the proportions of reagents that relate to the glassware solvent rinses received from the field.

10.2.3 The nominal final volume for a typical back-half composite sample extract is 400 mL, which includes the following reagent volumes:

- 8 mL of 0.5 µg/mL IDA
- 176 mL of methanol / 5% ammonium hydroxide (includes field solvent rinse
- 176 mL of reagent water / 5% ammonium hydroxide
- 40 mL of 2% formic acid

10.2.4 The XAD®-2 traps are emptied into an appropriate Nalgene container for preparation.

10.2.5 The XAD®-2 resin samples are spiked with the appropriate volume of IDA (typically 8.0 mL). The XAD®-2 samples undergo a dual extraction process; therefore approximately half of the back-half solvent rinse is added to the XAD®-2 for the first extraction. The remaining rinse is saved for later addition during the second extraction cycle. Additional extraction solvent (CH_3OH / 5% NH_4OH) is added to the extraction container to bring the volume up to a total of 88 mL minimum (or more in 22 mL increments).

10.2.6 A XAD®-2 method blank and XAD®-2 Laboratory Control Sample (LCS) are required to be included with this preparation batch. The LCS is spiked with both IDA and native HFPO-DA. Therefore, an additional 8 mL of a 0.5 µg/mL HFPO-DA native spike is added to the LCS prior to the addition of extraction solvent.

10.2.7 Samples are extracted on a shaker table for a minimum of 18 hours.

10.2.8 After the first 18 hour extraction cycle is completed for the samples, the extraction solvent is decanted into an appropriate labeled Nalgene container and set aside for combination with the later solvent extraction fluid.

10.2.9 The remaining back-half solvent rinse sample received from the field is added to the XAD®-2 sample from the shaker table followed by the addition of an appropriate volume of extraction solvent to bring it up to a total of 88 mL minimum (or more in 22 mL increments).

10.2.10 Repeat the second extraction with fresh solvent on a shaker table for a minimum of 18 hours.

10.2.11 After the second extraction cycle of back-half samples is completed, the solvent from both extraction cycles are combined with the XAD®-2 media.

10.2.12 Reagent water / 5% ammonium hydroxide is then added to the sample to bring it to a 1:1 ratio with extraction solvent (e.g. 176 mL methanol / 5% ammonium hydroxide: 176 mL reagent water / 5% ammonium hydroxide).

10.2.13 A 2% formic acid solution is finally added to each sample to provide a ratio of 5 mL 2% formic acid for each 22 mL of methanol / 5% ammonium hydroxide extraction solvent. Each sample is then mixed thoroughly.

10.2.14 Approximately 5-6 mL of the final back-half composite sample extract is filtered through a 0.45 µm polyethylene disk using a disposable, plastic syringe. The remainder of the sample extract portions is archived in an appropriate refrigerator.

10.3 Surface Wipe Samples

10.3.1 The nominal final volume for a Surface wipe sample extract is 50 mL, which includes the following reagents:

- 1 mL of 0.5 ug/mL IDA
- 22 mL of methanol / 5% ammonium hydroxide
- 22 mL of reagent water / 5% ammonium hydroxide
- 5 mL of 2% formic acid

10.3.2 **Note:** If 22 mL of extraction solvent (methanol / 5% ammonium hydroxide) is not enough to cover the wipe and allow the liquid to freely flow while shaking, an additional 22 mL of the extraction solvent, along with an additional 1 mL of IDA, is added to the container. Additional increments of the extraction solvent may be added until sufficient coverage is achieved for the extraction process to proceed properly.

10.3.3 The surface wipe samples are individually placed into an appropriate Nalgene container for preparation.

10.3.4 The surface wipe samples are spiked with the appropriate amount of IDA and the extraction solvent (CH_3OH / 5% NH_4OH) is added to the extraction container.

10.3.5 A surface wipe method blank and LCS are required for this preparation. Note that an additional 1 mL portion of a 0.5 µg/mL HFPO-DA native spike is added to the LCS prior to the addition of extraction solvent.

10.3.6 Samples are extracted on a shaker table for a minimum of 18 hours.

10.3.7 After extraction of the surface wipe samples is completed, the extraction solvent is transferred to a separate appropriate Nalgene container using a clean methanol-rinsed metal funnel (no filter paper is necessary)

10.3.8 Use a glass rod or the end of a disposable pipet to press the extracted surface wipe gauze against the bottom of the funnel to press out as much extraction solvent as reasonable from the surface wipe media.

10.3.9 Reagent water / 5% ammonium hydroxide solution is added to the sample to bring it into a 1:1 ratio with extraction solvent (e.g. 22 mL methanol / 5% ammonium hydroxide requires 22 mL reagent water / 5% ammonium hydroxide).

10.3.10 A 2% formic acid solution is added to each sample at a ratio of 5 mL 2% formic acid: 22 mL of methanol / 5% ammonium hydroxide extraction solvent. Each sample is then mixed thoroughly.

10.3.11 Approximately 5-6 mL of each surface wipe sample extract is filtered through a 0.45 µm polyethylene disk using a disposable, plastic syringe. The remainder of the sample extract portions is archived in an appropriate refrigerator.

10.4 Condensate samples

10.4.1 In order to calculate the total mass of HFPO-DA present in an individual Condensate Sample, the volume of liquid condensate as received is measured and recorded. The data is entered into a TALS batch in the "Vol Collected" column.

10.4.2 Routinely, the initial volume of Condensate sample processed in extraction is $1/20^{th}$ of the total condensate volume. After the total volume is determined, $1/20^{th}$ of the condensate sample is diluted to 250 mL using D.I. water. The volume of Condensate sample used is recorded in the TALS batch in the "Vol Cond. Used" column. The remaining sample is archived in refrigerated storage.

10.4.3 The diluted sample portion is shipped to the Denver Laboratory for extraction using SOP DV-OP-0019, section 10.5.

10.5 Sample Analysis

Extracted samples are shipped to the Denver Laboratory for analysis of HFPO-DA following SOP DV-LC-0012.

11.0 CORRECTIVE ACTION

When circumstances are encountered that are not specifically delineated in the analytical SOP or the corrective actions listed do not adequately address, a Non-Conformance Memo (NCM) will be initiated and the analyst should use his/her best analytical judgment and available resources to determine the best corrective action to be taken. The situation may be caused by more than one variable. The analyst should report the incident and seek the assistance from

his/her immediate supervisor, QA manager or other experienced staff. The analysis of project samples should not be resumed until the source of the problem and an in-control status is re-established. All samples associated with this should be reanalyzed after in-control status has been re-established or if authorization is received from the supervisor or QA Manager for release with data qualification. See SOP KNOX-QA-0008 for guidance on Non-Conformance procedures.

12.0 CALCULATIONS / DATA REDUCTION

12.1 Concentration, µg/Sample = C x V x Df x Fraction of sample extracted *

Where:

C = sample concentration in extract (µg/L)

V = Volume of extract (L)

Df = Dilution Factor

12.1.1 Example calculations per fraction at the reporting limit (where the calibration reporting limit is 0.5 µg/L)

Particulate Filter & Surface Wipe = 0.5 µg/L x 0.050 L = 0.025 µg/sample

XAD®-2 = 0.5 µg/L x 0.40 L = 0.200 µg/sample

Condensate* = 0.5 µg/L x 0.005 L = 0.0025 µg/sample

- Particulate Filter & Surface Wipe prep = 1 sample / 50 mL
- XAD®-2 prep = 1 sample / 400 mL
- Condensate prep = 1 sample* / 5 mL

* Condensate Sample: adjustment is made for the total volume of sample as received, and the total volume used in the extraction (e.g. if 1 sample = 200 mL, and 10 mL is extracted, then RL increases by 200/10 = 20x).

12.2 Documentation and Record Management

12.2.1 All sample preparation and analytical batch information, including the batch number(s), a list of samples being prepped, preparation analyst and date, identifications and amounts of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes) are recorded in TALS.

12.2.2 Raw data is scanned or saved directly as a PDF and is attached to the analytical batch in TALS.

12.2.3 The initial batch review is performed by the analyst and a second-level review is performed by the area supervisor or designee.

13.0 METHOD PERFORMANCE

13.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with SOP CA-Q-S-006. The laboratory maintains the MDL study records for analyses performed; these are verified quarterly (or when samples are extracted/analyzed).

13.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for these analyses, prior to testing client samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures that are used to analyze samples, including the sample preparation steps. The concentration of QC check samples should be approximately equivalent to a mid-level calibration point.

13.2.2 Calculate the average recovery percentage and standard deviation of the recovery percentage for each analyte of interest.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be reevaluated. TNI 2009 requires that the analyst achieve consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to carefully evaluate the analytical procedure and take corrective action.

13.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

13.2.5 Further details concerning demonstrations of proficiency are described in SOP KNOX-QA-0009.

13.3 Training Requirements

The Group Leader is responsible for ensuring that this proficiency demonstration procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must work under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under on-going supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP KNOX-QA-0009.

14.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity

needed, preparation of reagents based on anticipated usage and reagent stability). See KNOX-HS-0005, Waste Minimization Program. Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.0 WASTE MANAGEMENT

Waste management practices are conducted that are consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to KNOX-HS-0002.

15.1 The following waste streams are produced when this method is carried out:

15.1.1 Methanol waste – Flammable Solvent waste stream

15.1.2 Acidic waste – Acid waste stream

15.1.3 Caustic waste – Caustic waste stream

15.1.4 Solid waste generated by this procedure such as disposable pipette tips and extraction bottles are collected and turned into the Waste Coordinator for incineration in the incineration waste stream containers.

15.1.5 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

16.0 REFERENCES / CROSS-REFERENCES

16.1 DV-LC-0012 "Analysis of Perfluorooctanoic Acid (PFOA) and other Perfluorinated Hydrocarbons (PFCs) and Perfluorinated Hydrocarbon Sulfonates (PFSs) in Water and Soil by LC/MS/MS"

16.2 DV-OP-0019 "Extraction of Perfluorooctanoic Acid (PFOA) and Perfluorooctanoic Sulfonate (PFOS) and other Perfluorinated Hydrocarbons (PFCs) in Water and Soil"

16.3 EPA Method 0010 "Modified Method 5 Sampling Train"

16.4 EPA Method 3542A "Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)"

16.5 KX-QAM "Quality Assurance Manual

16.6 KNOX-QA-0008 "Nonconformance and Corrective Action"

16.7 KNOX-QA-0009 "Personnel Orientation and Training"

16.8 KNOX-HS-0002 "Waste Handling Procedures"

16.9 KNOX-HS-0005 "Waste Minimization Program"

16.10 CA-Q-S-006 "Detection and Quantitation Limits"

16.11 CW-E-M-001 Corporate "Environmental Health and Safety Manual"

17.0 METHOD MODIFICATIONS / CLARIFICATIONS

This procedure has been developed and optimized for the expressed purpose of deriving best practices for the characterization of HFPO-DA from flue gases sampled with Method 0010 sampling trains. Removal of HFPO-DA requires the use of methanol as an extraction fluid, and matrix matching for the utilization of EPA Method 8321A (LC/MS/MS). Other laboratory modifications may be necessary as required by changes to the sampling train made by the field team. This SOP presents the best practices demonstrated during the method development process, such as the most effective solvent system used to extract the various sampling train fractions, and need for a double extraction cycle of the XAD®-2 fraction to increase the extraction efficiency.

18.0 TABLES/ATTACHMENTS

Table 1: Standard Reporting Limits

Table 2: Reagent Ratio Guide

Attachment 1: Example bench extraction sheet

19.0 REVISION HISTORY

Revision 0, dated July 23, 2018

Table 1: Standard Reporting Limits

	Condensate (µg/sample)	Filter (µg/sample)	XAD®-2 (µg/sample)	Wipe (µg/sample)
HFPO-DA	0.0025	0.025	0.200	0.025

See section 12.1 for nominal initial/final volume

Table 2: Method 0010 Reagent Ratio Guide

Probe & Nozzle Rinse Volume as Received From the Field (CH_3OH / 5% NH_4OH)	Adjusted Volume (CH_3OH / 5% NH_4OH)	IDA Spike Volume $^{13}C_3$-HFPO-DA (0.5 µg/mL)	H_2O / 5% NH_4OH Volume Added	Formic Acid Volume Added	Final Extract Prepared Volume
< 22 mL	22 mL	1 mL	22 mL	5 mL	50 mL
< 44 mL	44 mL	2 mL	44 mL	10 mL	100 mL
< 66 mL	66 mL	3 mL	66 mL	15 mL	150 mL
< 88 mL	88 mL	4 mL	88 mL	20 mL	200 mL
< 110 mL	110 mL	5 mL	110 mL	25 mL	250 mL
< 132 mL	132 mL	6 mL	132 mL	30 mL	300 mL
< 154 mL	154 mL	7 mL	154 mL	35 mL	350 mL
< 176 mL	176 mL	8 mL	176 mL	40 mL	400 mL

Attachment 1: Example extraction bench sheet

TestAmerica Knoxville Extraction Sheet
HFPO-DA in Source Air Front Half Fraction

Batch Number: _____
TALS Prep Chain: LCMS_FH_Prep

Sample ID	Measure associated rinses using a graduated cylinder and record volume (mL)	Push down filter with tweezers in bottle	Create MB and LCS by using clean filter and placing in 125mL container	Add 0.5 µg/mL IS (IDA) to all samples & QC. Record volume in TALS.	Add 0.5 mg/mL native spike (TA) to LCS. Record volume in TALS.	Add rinses and MeOH/5% NH4OH to the appropriate volume. Record volume of extraction solvent (mL)	Extract on shaker table for 16hr minimum	Filter sample using filter paper and plastic funnel	Add the appropriate volume of reagent H20/5% NH4OH. Record volume (mL).	Add the appropriate volume of 2% formic acid solution. Record volume (mL).	Filter approximately 5-6mL using plastic syringe and 0.45µm PVDE filter disk.

OP135R0, 3/29/18 OP135R0 HFPO_DA Front Half (TALS).xls

Attachment 1: Example extraction bench sheet (continued)

TestAmerica Knoxville Extraction Sheet
HFPO-DA in Source Air Back Half Fraction

Batch Number: _____
TALS Prep Chain: LCMS_BH_Prep

Sample ID	Measure associated rinses using a graduated cylinder and record volume (mL)	Create MB and LCS by using clean XAD and placing in 500mL Nalgene container	Empty all XAD from traps into 500mL Nalgene containers	Add 0.5 µg/mL IS (IDA) to all samples & QC. Record volume in TALS.	Add 0.5 mg/mL native spike (TA) to LCS. Record volume in TALS.	Add rinses and MeOH/5% NH4OH to the appropriate volume. Record volume of extraction solvent (mL)	Extract on shaker table for 18hr minimum	Decant solvent from 1st extraction into a separate Nalgene container	Add remaining rinses and MeOH/5% NH4OH to the appropriate volume. Record volume of extraction solvent (mL)	Combine 1st extraction solvent with the XAD sample	Add the appropriate volume of reagent H20/5% NH4OH. Record volume (mL).	Add the appropriate volume of 2% formic acid solution. Record volume (mL).	Filter approximately 5-6mL using plastic syringe and 0.45µm PVDF filter disk.

GP136R0, 4/2/18 OP136R0 HFPO_DA Back Half (TALS).xlsx