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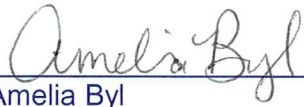

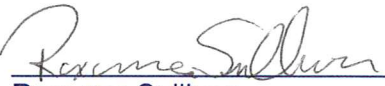
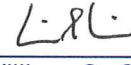
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**Title: Extraction of Perfluorooctanoic Acid (PFOA) and
Perfluorooctanoic Sulfonate (PFOS) and other Perfluorinated
Hydrocarbons (PFCs) in Water and Soil**

Approvals (Signature/Date):

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1.0 Scope and Application

- 1.1 This procedure describes the extraction of perfluorooctanoic acid (PFOA, CAS# 335-67-1), and perfluorooctanoic sulfonate (PFOS, no CAS number), and other Perfluorinated Hydrocarbons (PFC's) from water and soil samples. The method has been validated by TestAmerica Denver for reagent water, drinking water, groundwater, and soil. See Table 1 for analytes that can be extracted under this procedure.
- 1.2 This procedure does not describe the LC/MS/MS analysis of the extracts. For those details, see DV-LC-0012 "*Analysis of Perfluorooctanoic Acid (PFOA), Perfluorooctanoic Sulfonate (PFOS), and other Perfluorinated Hydrocarbons (PFCs) by LC/MS/MS*"

2.0 Summary of Method

- 2.1 For all compounds except perfluorooctane sulfonamide (FOSA), water samples undergo solid phase extraction using a Strata X-AW 33u Polymeric Weak Anion cartridge. The compounds are eluted from the cartridge with a 10% ammonium hydroxide in methanol solution.
- 2.2 For perfluorooctane sulfonamide (FOSA), water samples undergo solid phase extraction using a Waters tC18 cartridge. FOSA is eluted from the cartridge with methanol.
- 2.3 Soil samples are mixed with a sodium hydroxide solution and allowed to sit for 1/2 hour. Methanol is then added and the soil/solvent mixture is tumbled for 24 hours. The pH is adjusted to ≤ 7 then the mixture is centrifuged and the solvent filtered. The extract is then brought up to final volume with methanol. This extraction procedure is used for all PFCs.
- 2.4 Labeled PFC's are used in this analysis as an isotope dilution standard. The isotope dilution technique allows correction for analytical bias encountered when analyzing more chemically complex environmental samples. A known quantity of the labeled PFC compounds is added to every sample and to the batch quality control samples prior to extraction. Because the isotopically labeled compound is chemically similar to the compound of concern, it is affected by any interfering substances in the sample to the same extent as the compound of concern. The recovery of the labeled PFC's is then used to mathematically correct the final results for the PFC's.

3.0 Definitions

Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, Quality Control Program, for definitions of general analytical and QA/QC terms.

- 3.1 **PTFE:** polytetrafluoroethylene (e.g., Teflon®)

- 3.2 Preparation Batch: A group of up to 20 samples that are of the same matrix and are processed together in the same extraction event using the same procedure and lots of reagents and standards
- 3.3 Method Comments: The Method Comments are used to communicate to the bench level chemists special requirements and instructions from the client. Please reference WI-DV-0032 for details on Method Comments.
- 3.4 Quality Assurance Summary (QAS): Certain clients may require extensive specific project instructions or program QC, which are too lengthy to fit conveniently in the Method Comments field in LIMS. In these situations, laboratory Project Managers describe the special requirements in a written QAS to address these requirements. QASs are posted on a public drive for easy accessibility by all lab employees. Normally, QASs are introduced to analysts in an initial project kick-off meeting to be sure that the requirements are understood.
- 3.5 Aliquot: A part that is a definite fraction of a whole; as in “take an aliquot of a sample for testing or analysis.” In the context of this SOP, “aliquot” is also used as a verb, meaning to take all or part of a sample for preparation, extraction, and/or analysis.

4.0 **Interferences**

- 4.1 PFCs have been used in a wide variety of manufacturing processes, and laboratory supplies should be considered potentially contaminated until they have been tested and shown to be otherwise. The materials and supplies used during the method validation process have been tested and shown to be clean. These items are listed below in Section 6.
- 4.2 To avoid contamination of samples, standards are prepared in a ventilation hood in an area separate from where samples are extracted.
- 4.3 PTFE products can be a source of PFOA and PFC contamination. The use of PTFE in the procedure should be avoided or at least thoroughly tested before use.
- 4.4 Volumetric glassware and syringes are difficult to clean after being used for solutions containing high levels of PFOA and PFCs. These items should be labeled for use only with similarly concentrated solutions or verified clean prior to re-use. To the extent possible, disposable labware is used.
- 4.5 Aluminum foil and foilware has been identified as a possible source of PFOA and PFC contamination. These materials should be avoided during the extraction process.
- 4.6 PFOA and PFCs can readily adhere to glass surfaces, glass containers should be avoided as much as possible during the extraction of the samples. Therefore water samples will be aliquoted gravimetrically instead of using volumetric glassware.

5.0 **Safety**

- 5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, 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 **Specific Safety Concerns or Requirements**
- 5.3.1 Preliminary toxicity studies indicate that PFOA and PFOS could have significant toxic effects. In the interest of keeping exposure levels as low as reasonably achievable, PFOA and PFOS must be handled in the laboratory as if they are hazardous and toxic chemicals.
- 5.3.2 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.
- 5.3.3 Stock standards are purchased as high purity solids in a powder form or at a certified concentration in solvent. Handling of the powder will be limited to making intermediate concentration standards in solution, which will be done only in certified laboratory fume hoods. The pure powders are stored in sealed bottles kept in cabinets with known or other presumed hazardous chemicals. There are no steps in this method that would generate mists in the open lab environment.
- 5.3.4 The melting point for PFOA is 53°C. Therefore, the vapor pressure is extremely low at ambient lab temperatures. As a result, inhalation of vapors during this procedure is not considered to be a significant health risk.
- 5.3.5 PFOA is an acid and is not compatible with strong bases.
- 5.3.6 PFOA and PFOS are not known to be highly flammable. However, methanol is highly flammable and is 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.

5.4 **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
Hydrochloric Acid	Corrosive Poison	5 ppm (Ceiling)	Can cause pain and severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause deep ulcerations to skin, permanent eye damage, circulatory failure and swallowing may be fatal.
Sodium Hydroxide	Corrosive Poison	2 mg/cm ³ (Ceiling)	Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.
Formic Acid	Combustible Corrosive Flammable	5 ppm (TWA)	Causes severe burns, toxic by inhalation, harmful if swallowed, possible sensitizer.
Methanol	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.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

All equipment IDs for any support equipment (pipettes, thermometers, etc.) must be recorded in the batch record.

6.1 Equipment

- 6.1.1 Vacuum manifold for SPE cartridges. Capable of maintaining approximately 66 cm (26”) of Hg. After each use, the valves are removed from the manifold and placed in a jar with acetonitrile. The jar is placed into a sonication bath overnight.
- 6.1.2 Bottle rotating apparatus for the extraction of soil samples.
- 6.1.3 Nitrogen evaporation apparatus (N-EVAP) for the concentration of some water extracts.

- 6.1.4 Balance capable of measuring ± 0.1 g. Calibration checked per SOP DV-QA-0014. Used to measure the initial sample mass and volume.
- 6.1.5 Pipettor with disposable 1.0 mL tips. Calibration checked per SOP DV-QA-0008. Used to add internal standard and spike solution to samples.
- 6.1.6 Pipettor with disposable 0.1 mL tips. Calibration checked per SOP DV-QA-0008. Used to add internal standard and spike solution to samples.
- 6.1.7 Pipettor capable of dispensing 5 to 50 mL. Calibration checked per SOP DV-QA-0008. Used to calibrate vials to hold 5 mL for the final volume determination for water extracts.
- 6.1.8 Pipettor capable of dispensing 0.6 to 5.6 mL. Calibration checked per SOP DV-QA-0008. Used to bring soil extracts to a 20 mL final volume.
- 6.1.9 Centrifuge capable of clarifying water samples and soil extracts that contain sediment.

6.2 Supplies

- 6.2.1 10-mL HDPE vials, screw thread – used to store final extracts.

NOTE: Vials used to store the final extracts of water samples are calibrated to hold a volume of 5 mL by using a calibrated pipette to deliver 5 mL of HPLC grade methanol into the vial and marking the meniscus with a fine tipped permanent marker. This volume is accurate to ± 2 %.

- 6.2.2 125 mL HDPE wide-mouth bottles – used in the extraction of soil samples.
- 6.2.3 Syringe filter, 0.45 μ m, PVDF, Millipore Millex-HV, or equivalent – used to filter soil extracts.
- 6.2.4 Strata X-AW 33u Polymeric Weak Anion 200 mg packed in 6 mL tubes, Phenomenex part no. 8B-S038-FCH (or equivalent) – used in the extraction of all PFCs described in Section 10.5, except FOSA. See Sections 6.2.5 and 10.6 for FOSA cartridge and extraction procedure.
- 6.2.5 Waters SPE cartridge “tC18” part number WAT036795 (or equivalent) – used in the extraction of FOSA that is described in Section 10.6.
- 6.2.6 SPE tubing, non-PTFE in composition, Tubing is cleaned before and after use with HPLC grade methanol and HPLC grade water.
- 6.2.7 Miscellaneous laboratory apparatus (beakers, test tubes, volumetric flasks, pipettes etc.). These should be disposable or HDPE where possible, glass should be avoided.

6.2.8 pH paper – wide range.

6.3 **Computer Software and Hardware**

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 **Reagents and Standards**

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1 HPLC Grade Methanol – Used in rinsing SPE lines and ports, in the making of standards, conditioning of SPE cartridges, the extraction of water samples for FOSA, and the extraction of soil samples.

7.2 Ottawa Sand – Used to prepare method blanks and LCSs for the extraction of soil samples. Ottawa Sand is baked at 400°C for at least 4 hours.

7.3 HPLC Grade Water – Used to prepare method blanks and LCSs for the extraction of water samples.

7.4 0.67 N NaOH solution – Used in the extraction of soil samples.

Using a Class A graduated cylinder, transfer 67 mL of 10 N NaOH to a 1000 mL Class A volumetric flask and bring to volume with HPLC grade water.

7.5 2.4 M HCl solution – Used in the extraction of soil samples.

Fill a 500 mL Class A volumetric flask approximately half full with HPLC grade water. Using a Class A graduated cylinder, transfer 100 mL of reagent grade concentrated HCL to the flask and then bring to volume (500 mL) with HPLC grade water.

7.6 10% Ammonium Hydroxide in Methanol – Used in the elution of PFOA, PFOS, and PFCs except FOSA from the Strata X-AW 33u Polymeric Weak Anion (or equivalent).

Fill a 1000 mL Class A volumetric flask approximately half full with HPLC grade methanol. Using a Class A graduated cylinder, transfer 100 mL of ammonium hydroxide to the flask and then bring to volume (1000 mL) with HPLC grade methanol.

7.7 5% Ammonium Hydroxide in 50/50 Water/Methanol – Used in the extraction of HFPO-DA from soils.

Transfer 50 mL of ammonium hydroxide into a 1000 mL Class A graduated cylinder. Bring to volume (1000 mL) with equal parts HPLC water/HPLC grade methanol.

7.8 2% Formic Acid – Used to rinse the Strata X-AW 33u Polymeric Weak Anion (or equivalent) in the extraction of PFOA, PFOS, and PFCs except FOSA. Also used to neutralize the pH in the extraction of HFPO-DA from soils.

Fill a 1000 mL Class A volumetric flask approximately half full with HPLC grade water. Using a Class A graduated cylinder, transfer 23 mL of 88% formic acid to the flask and bring to volume (1000 mL) with HPLC grade water.

7.9 Stock Standard Materials

7.9.1 The PFCs are purchased as a certified concentration in solution. Standard materials are verified compared to a second source material at the time of initial calibration.

7.9.2 Stock standard solutions are stored at 0-6°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 preparation.

7.9.3 All standards are stored in HDPE bottles and vials. Glass containers are avoided.

7.10 “PFOA/S_Spike”, 0.5 µg/mL

7.10.1 A spike solution is prepared containing PFOA and PFOS at 0.5 µg/mL each in HPLC grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.

7.10.2 For soil samples, when PFOA and PFOS are the only analytes of concern, 0.4 mL of this solution is spiked into the LCS and matrix spike samples, which results in a 20 µg/Kg sample concentration.

7.10.3 For water samples, when PFOA and PFOS are the only analytes of concern, 0.1 mL of this solution is spiked into the LCS and matrix spike samples, which results in a 0.2 µg/L sample concentration.

7.11 “PFC-LCS-BR”, 0.5 µg/mL

- 7.11.1 A spike solution is prepared containing all PFCs listed in Table 1 at 0.5 µg/mL each in LCMS grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.
- 7.11.2 For soils samples, when more PFCs than just PFOA and PFOS are the analytes of concern, 0.4 mL of this solution is spiked into the LCS and matrix spike samples, which results in a 20 µg/Kg sample concentration.
- 7.11.3 For water samples, when more PFCs than just PFOA and PFOS are the analytes of concern, 0.1 mL of this solution is spiked into the LCS and matrix spike samples, which results in a 0.2 µg/L sample concentration.

7.12 “FOSA-H2O-LCS”, 0.05 µg/mL

- 7.12.1 A spike solution is prepared containing only perfluorooctane sulfamide (FOSA) at 0.05 µg/mL in HPLC grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.
- 7.12.2 For water samples, when FOSA is the analyte of concern, 1 mL of this solution is spiked into the LCS and matrix spike samples, which results in a 0.2 µg/L sample concentration.

7.13 “PFOA/S_Surr/IS”, 0.5 µg/mL

- 7.13.1 An isotope dilution spike solution is prepared containing the internal standards 13C4 PFOA and 13C4 PFOS at 0.5 µg/mL in HPLC grade methanol. This standard also contains the surrogate compounds 13C8 PFOA and 13C8 PFOS at 0.5 µg/mL. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.
- 7.13.2 For soil samples, when PFOA and PFOS are the only analytes of concern, 0.4 mL of this standard is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 20 µg/kg spike concentration.
- 7.13.3 For water samples, when PFOA and PFOS are the only analytes of concern, 0.1 mL of this standard is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 0.2 µg/L spike concentration.

7.14 “PFC_Surr&IS”, 0.5 µg/mL

- 7.14.1 An isotope dilution spike solution is prepared containing all of the labeled PFC isotopes listed in Table 2 and the surrogate compounds listed in Table 3 at 0.5 µg/mL in HPLC grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.

7.14.2 For soil samples, when more PFCs than just PFOA and PFOS are the analytes of concern, 0.4 mL of this standard is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 20 µg/kg spike concentration.

7.14.3 For water samples, when more PFCs than just PFOA and PFOS are the analytes of concern, 0.1 mL of this standard is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 0.2 µg/L spike concentration.

7.15 “FOSA8-IS-SPK”, 0.05µg/mL

7.15.1 A spike solution is prepared containing only 13C8 FOSA at 0.05 µg/mL in HPLC grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.

7.15.2 For water samples, when FOSA is the analyte of concern, 1 mL of this solution is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 0.2 µg/L sample concentration.

7.16 “HFPO I.S”, 0.5 µg/mL

7.16.1 A spike solution is prepared containing only 13C3 HFPO-DA at 0.5 µg/mL in LCMS grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.

7.16.2 For water samples, when HFPO is the analyte of concern, 0.1 mL of this solution is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 0.2 µg/L sample concentration.

7.17 “HFPO Spike”, 0.5 µg/mL

7.17.1 A spike solution is prepared containing only HFPO-DA (Perfluoro(2-propoxypropanoic acid) at 0.5 µg/mL in HPLC grade methanol. This standard is stored in HDPE bottles at 0-6°C and given a 1 year expiration date.

7.17.2 For water samples, when HFPO is the analyte of concern, 0.1 mL of this solution is added into each sample (field and laboratory QC samples) at the beginning of the preparation. This produces a 0.2 µg/L sample concentration.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client

requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time ¹	Analytical Holding Time	Reference
Waters	HDPE ²	250 mL (x2) ³	Cool, ≤ 6°C	14 Days	40 Days	N/A ⁴
Soils	HDPE	10 g	Cool, ≤ 6°C	14 Days	40 Days	N/A ⁴

¹ Extraction holding times were determined based on stability studies performed during the development of this method. TestAmerica Denver has conducted stability studies indicating that medium- and low-level standard solutions of PFOA are stable for at least two months in glass, polystyrene, and polypropylene plastics at 0-6 °C.

² PFCs have been shown to adhere to glass. Glass containers are not an appropriate sample collection vessel.

³ If FOSA is a target analyte for a specific client's samples in addition to other PFCs, duplicate water samples are required because FOSA is extracted separately and therefore 2-250 mL bottles are required.

⁴ This method was developed and validated by TestAmerica Denver.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply. For SOPs that address only preparation, QC acceptance limits on the analytical results are not included. Refer to the appropriate SOP that describes the determinative method.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

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

9.1.4 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 DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 12 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. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

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

9.4.1 The method blank for batches of aqueous samples consists of 250 mL of HPLC grade water free of any of the analyte(s) of interest.

9.4.2 The method blank for batches of soil samples consists of 10 g of baked Ottawa sand free of any of the analyte(s) of interest.

9.5 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD)

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. When an MS/MSD pair is not available, an LCS and LCSD are required.

9.5.1 For aqueous sample batches, the LCS consists of 250 mL of HPLC grade water free of any of the analyte(s) of interest.

9.5.2 For soil sample batches, the LCS consists of 10 g of baked Ottawa sand free of any of the analyte(s) of interest.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

9.6.2 If insufficient sample volume is available for MS/MSD, an NCM must be written and a LCSD must be prepared.

9.7 Isotopically Labeled Internal Standard (IS)

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

9.8 Surrogate Standard

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

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an 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 # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 All glassware and positions must be rotated through both QC and field samples. **Do not** use specific glassware or positions for the MB and LCS/LCSD.

10.4 All equipment IDs for any support equipment (pipettes, thermometers, etc.) used **must** be recorded in the batch record.

10.5 **Water Sample Extraction for PFOA/PFOS, HFPO-DA, and Full List PFCs, not including FOSA**

- 10.5.1** The procedure described here in Section 10.5 is for water samples that are to be analyzed for PFOA or PFOS only (Prep method 3535 with analytical method LCMS_PFOA or analytical method 8321A_PFC_Du), the full-list of PFCs (Prep method 3535 with analytical method PFC), or HFPO-DA only (prep method 3535 with analytical method 8321A_HFPO_Du). If the sample requires the analysis of FOSA it will be logged in with the prep method 3535_FOSA and the procedure in Section 10.6 should be followed instead.
- 10.5.2** The routine sample volume used is 250 mL. Samples should be received from the client in un-preserved HDPE plastic bottles. If samples are received in glass containers, then an NCM should be written to document the deviation from the procedure.
- 10.5.3** Inspect the water sample for the presence of sediment. The sample must be free of particulate matter before it is introduced into the SPE extraction cartridge. Particulate matter will obstruct the media and cause the analysis to fail. Samples should NOT be filtered through glass fiber filter paper prior to extraction. PFOA and PFOS are known to adhere to glass so filtering the sample should only be performed after the extraction has been attempted and has failed and only with client approval.
- 10.5.4** If the water sample contains visible sediment or particulate matter, make sure that all particulate matter has settled to the bottom of the sample container and take care not to disturb or re-suspend the particulate matter. If necessary, centrifuge the sample to pull the particulate down to the bottom of the container.
- 10.5.5** The sample may be extracted directly from the sample container, or the sample can be transferred to a 250 mL HDPE bottle.
- 10.5.5.1** If the sample is transferred to a HDPE bottle, place the HDPE bottle on a balance and tare. Then carefully pour the sample from the original container into the tared HDPE bottle, making sure that if any sediment is present, it is not transferred to the bottle. Stop pouring when the balance read out is between 250 g to 275 g. Record the balance readout as the initial sample volume in mL on the benchsheet.
- NOTE:** Some clients specifically disallow decanting the sample. If this is the case and sediment is present, an NCM must be written to document that the client requirements could not be followed due to the sediment in the sample that would interfere with the analysis.
- 10.5.5.2** If the sample is extracted directly from the original sample container, weigh the full original sample bottle to the nearest gram using a top loading balance, and record the weight on the benchsheet. After the extraction, weigh the empty sample bottle, and record the weight. Subtract the empty bottle weight from the

full bottle weight and record the difference as the sample volume in mL.

NOTE: Some client specifically disallow aliquoting the sample gravimetrically and instead require the sample to be aliquoted volumetrically. Because the PFCs are known to adhere to glass and because of the possible cross-contamination that can occur with the use of Class A graduated cylinders, samples for this procedure are NOT aliquoted volumetrically. Prepare an NCM to document why the Method Comments were not followed.

- 10.5.6** Prepare any requested MS/MSD and duplicate samples by measuring additional sample aliquots. If the client has not requested any MS/MSD or duplicate samples, then a sample should be chosen at random for the MS/MSD as long as there is sufficient sample volume to do so.
- 10.5.7** Prepare MB and LCS samples by measuring 250 mL of HPLC grade water into a 250 mL HDPE bottle. One MB should be performed per batch. At least one LCS should be performed per batch. If there was insufficient sample volume to perform a matrix spike duplicate (MSD) or a sample duplicate, then a Laboratory Control Sample Duplicate (LCSD) must be performed.
- 10.5.8** Using a calibrated pipette, add 0.1 mL of the correct IS/Surrogate standard to every sample and every MS/MSD, duplicate, MB and LCS/LCSD sample. To determine the correct internal standard solution, check the prep and analytical method logged and reference WI-DV-0009.
- 10.5.8.1** If the sample is logged for prep method 3535 with an analytical method of LCMS_PFOA or an analytical method of 8321A_PFC_Du, then the analytes of interest include PFOA and PFOS only and 0.1 mL of the "PFOA/S_Sur/IS", solution described in Section 7.13 should be used.
- 10.5.8.2** If the sample is logged for prep method 3535 with an analytical method of PFC, then the analytes of interest include additional PFC compounds and the "PFC_Surr&IS", solution described in Section 7.14 should be used.
- 10.5.8.3** If the sample is logged for prep method 3535 with an analytical method of 8321A_HFPO_Du, then the analytes of interest include HFPO only and the "HFPO I.S." solution described in section 7.16 should be used.
- 10.5.8.4** If the sample is logged for prep method 3535_FOSA, then the procedure in Section 10.6 should be followed instead of this procedure.

NOTE: The addition of all spikes and surrogates should be done immediately following a review by a 2nd analyst. See WI-DV-0009.

- 10.5.9** Using a calibrated pipette, add 0.1 mL of the correct spike standard to every MS/MSD and the LCS samples. To determine the correct spike standard solution, check the prep and analytical method logged and reference WI-DV-0009.
- 10.5.9.1** If the sample is logged for prep method 3535 with an analytical method of LCMS_PFOA, or analytical method 8321A_PFC_Du then the analytes of interest include PFOA and PFOS only and the "PFOA/S_Spike" solution described in Section 7.9.3 should be used.
- 10.5.9.2** If the sample is logged for prep method 3535 with an analytical method of PFC, then the analytes of interest include additional PFC compounds and the "PFC-LCS-BR" solution described in Section 7.11 should be used.
- 10.5.9.3** If the sample is logged for prep method 3535 with an analytical method of 8321A_HFPO_Du, then the analytes of interest includes HFPO only and the "HFPO Spike" solution described in section 7.17 should be used.
- 10.5.9.4** If the sample is logged for prep method 3535_FOSA, then the procedure in Section 10.6 should be followed instead of this procedure.
- 10.5.10** Cap and shake each sample to ensure the surrogate and spike compounds are incorporated into the sample matrix. If necessary, centrifuge the sample to separate any suspended sediment that is suspended.
- 10.5.11** Rinse each vacuum manifold port and line once with HPLC grade methanol and once with HPLC grade water. Care should be taken not to use lines made from PTFE.
- 10.5.12** Pre-condition the Strata X-AW 33u Polymeric Weak Anion cartridges (or equivalent) with 12 mL of HPLC grade methanol by filling the cartridge two times with HPLC grade methanol and drawing it through the cartridge using a vacuum manifold.
- 10.5.13** Condition the SPE cartridge with 24 mL of HPLC grade water by filling the cartridge four times and drawing the water through the cartridge using a vacuum manifold. Fill the cartridge a fifth time and close the valve to prevent the water from dripping through and making sure the packing is wet.
- 10.5.14** After conditioning, cap each cartridge. Make sure the cap is clean and rinsed free of solvent with HPLC grade water.

- 10.5.15** Using the tubing that has been rinsed with HPLC grade methanol and HPLC grade water, connect the cartridge to the sample container. The tubing should NOT be made of PTFE. If the extraction is being performed directly from the sample container care should be taken if there are solids that have settled to the bottom of the bottle. If necessary, use a centrifuge to pull sediment to the bottom of the sample container and clip the tubing so that the end is not resting on the bottom, but suspended above the solids. Secure the bottles to each other with rubber bands in groups of 3 or 4 so that as the sample is drawn out of the bottle the weight of the tubing does not cause them to tip over.
- 10.5.16** Turn on the vacuum and open the valves slowly so that the sample is drawn through the cartridge at a rate of approximately 4 mL /minute. The solution should come out of the cartridge as individual drops. If the sample comes out of the cartridge in a stream instead of drops, the extraction rate is too fast. The extraction should take approximately 1 hour to complete, however a slower drip rate is not detrimental to the extraction.
- 10.5.17** A cartridge is considered clogged if a flow rate of 4 mL/min cannot be achieved. If the cartridge clogs during sample loading, a second cartridge can be used for the sample and then extracts are combined. Alternatively, measure the amount of sample successfully extracted, and use that volume for the extraction constant. If this approach is used, then the surrogate and spike volumes must be corrected for the new initial volume. See Section 11 on how to calculate the actual surrogate and spike volumes.
- 10.5.18** As the sample level in the container drops, rinse the walls of the container with HPLC water. If a clip was used to keep the end of the line off of the bottom of the sample bottle and away from solids, lower it at this point in an attempt to extract the entire sample. If there is so much sediment that rinsing will cause the sediment to clog the cartridge, write an NCM stating the rinse could not be performed. After all of the sample and the water used to rinse the container has gone through the line, close the valve and remove the line and the cap from the cartridge. If the valve was not closed before the cartridge went dry, re-hydrate the packing as soon as possible with reagent water. It is important not to leave the cartridge packing dry, but do not leave any water remaining above the glass frit that sits on top of the column packing.
- 10.5.19** After all samples have passed through the cartridge and valves have been closed and all lines and caps have been removed from the cartridges, rinse each cartridge once with 6 mL of the 2% formic acid solution described in Section 7.8. Open the valves and draw the formic acid solution through with the vacuum. Do not allow the cartridge to go dry, but do not leave any solution remaining above the glass frit that sits on top of the column packing.
- 10.5.20** Rinse each cartridge with HPLC Grade methanol by filling the cartridges once with 6 mL of methanol and opening the valves and drawing it through with the vacuum. Do not allow the cartridge to go dry, but do not leave any

solution remaining above the glass frit that sits on top of the column packing.

- 10.5.21** Turn off the vacuum and remove the manifold lid. Rinse the needles on the underside of the manifold lid with a lab tissue that has been wetted with HPLC grade methanol. Care should be taken not to cross-contaminate the samples during this step. Place it to the side on a clean lab tissue. Place the vial holder inside the manifold and place 8 mL HDPE vials that have been calibrated to 5 mL inside the manifold on top of the vial holder. Replace the manifold lid and be sure that each valve needle is positioned inside a vial.
- 10.5.22** Using a bottle-top pump add 4 mL of the 10% ammonium hydroxide in methanol solution described in Section 7.6 to each cartridge. Turn on the vacuum pump while the valves on the manifold are still closed, then quickly open and close each valve to create a vacuum in the cartridges. Turn off the vacuum pump and open the manifold valve to break the vacuum in the manifold. Open the valves to allow the ammonium hydroxide to drip gravimetrically.
- 10.5.23** After the solution has stopped dripping, reapply the vacuum to ensure that the last portion of solution is collected. This is a very important step.
- 10.5.24** If two cartridges were used, transfer all extracts into one collection vial and evaporate down to approximately 4 mL using an N-Evap. Continue to the next step.
- 10.5.25** Add HPLC grade water to the extract in the sample collection vial until the meniscus reaches the 5.0-mL mark.
- 10.5.26** The water sample extracts are ready for analysis. See SOP DV-LC-0012 for details on the analysis.
- 10.5.27** See Section 14.0 for proper disposal of all waste.

10.6 Water Sample Extraction for FOSA by 3535_FOSA

- 10.6.1** Inspect the water sample for the presence of sediment. The sample must be free of particulate matter before it is introduced into the SPE extraction cartridge. Particulate matter will obstruct the media and cause the analysis to fail. Samples should NOT be filtered through glass fiber filter paper prior to extraction. PFCs are known to adhere to glass so filtering the sample should only be performed after the extraction has been attempted and has failed and only with client approval.
- 10.6.2** If the water sample contains visible sediment or particulate matter, make sure that all particulate matter has settled to the bottom of the sample container and take care not to disturb or re-suspend the particulate matter. If necessary, centrifuge the sample to pull the particulate down to the

bottom of the container.

10.6.3 The sample may be extracted directly from the sample container, or the sample can be transferred to a 250 mL HDPE bottle.

10.6.3.1 If the sample is transferred to a HDPE bottle, place the HDPE bottle on a balance and tare. Then carefully pour the sample from the original container into the tared HDPE bottle, making sure that if any sediment is present, it is not transferred to the bottle. Stop pouring when the balance read out is between 250 g to 275 g. Record the balance readout as the initial sample volume in mL on the benchsheet.

NOTE: Some client requirements specifically disallow decanting the sample. If this is the case and sediment is present, an NCM must be written to document that the client requirements could not be followed due to the sediment in the sample that would interfere with the analysis.

10.6.3.2 If the sample is extracted directly from the original sample container, weigh the full original sample bottle to the nearest gram using a top loading balance, and record the weight on the benchsheet. After the extraction, weigh the empty sample bottle, and record the weight. Subtract the empty bottle weight from the full bottle weight and record the difference as the sample volume in mL.

NOTE: Some client specifically disallow aliquoting the sample gravimetrically and instead require the sample to be aliquoted volumetrically. Because the PFCs are known to adhere to glass and because of the possible cross-contamination that can occur with the use of Class A graduated cylinders, samples for this procedure are NOT aliquoted volumetrically. Prepare an NCM to document why the Method Comments were not followed.

10.6.4 Prepare any requested MS/MSD and duplicate samples by measuring additional sample aliquots. If the client has not requested any MS/MSD or duplicate samples, then a sample should be chosen at random for the MS/MSD as long as there is sufficient sample volume to do so. When an MS/MSD pair is not available, an LCS and LCSD are required.

10.6.5 Prepare MB and LCS samples by measuring 250 mL of HPLC grade water into a 250 mL HDPE bottle. One MB should be performed per batch. At least one LCS should be performed per batch. If there was insufficient sample volume to perform a matrix spike duplicate (MSD) or a sample duplicate, then a Laboratory Control Sample Duplicate (LCSD) should be performed.

- NOTE:** The addition of all spikes and surrogates should be done immediately following a review by a 2nd analyst. See WI-DV-0009.
- 10.6.6** Using a calibrated pipette, add 1.0 mL of the “FOSA8-IS-SPK” solution described in Section 7.14.3 to all samples and all QC samples.
- 10.6.7** Using a calibrated pipette, add 1.0 mL of the “FOSA-H2O-LCS” solution described in Section 7.12 to every MS/MSD and to the LCS samples.
- 10.6.8** Cap and shake each sample to ensure the surrogate and spike compounds are incorporated into the sample matrix. If necessary, centrifuge the sample to separate any suspended sediment that is suspended.
- 10.6.9** Rinse each vacuum manifold port and line once with HPLC grade methanol and once with HPLC grade water. Care should be taken not to use lines made from PTFE.
- 10.6.10** Pre-condition the Waters tC18 SPE cartridge (or equivalent) with 12 mL of HPLC grade methanol by filling the cartridge two times with methanol and drawing it through the cartridge using a vacuum manifold.
- 10.6.11** Condition the SPE cartridge with approximately 24 mL of HPLC grade water by filling the cartridge four times and drawing the water through the cartridge using a vacuum manifold. Fill the cartridge a fifth time and close the valve to prevent the water from dripping through and making sure the packing is wet.
- 10.6.12** After conditioning, cap each cartridge. Make sure the cap is clean and rinsed free of solvent with HPLC grade water.
- 10.6.13** Using the tubing that has been rinsed with HPLC grade methanol and HPLC grade water, connect the cartridge to the sample container. The tubing should NOT be made of PTFE. If the extraction is being performed directly from the sample container care should be taken if there are solids that have settled to the bottom of the bottle. If necessary, use a centrifuge to pull sediment to the bottom of the sample container and clip the tubing so that the end is not resting on the bottom, but suspended above the solids. Secure the bottles to each other with rubber bands in groups of 3 or 4 so that as the sample is drawn out of the bottle the weight of the tubing does not cause them to tip over.
- 10.6.14** Turn on the vacuum and open the valves slowly so that the sample is drawn through the cartridge at a rate of approximately 4 mL/minute. The solution should come out of the cartridge as individual drops. If the sample comes out of the cartridge in a stream instead of drops, the extraction rate is too fast. The extraction should take approximately 1 hour to complete, however a slower drip rate is not detrimental to the extraction.
- 10.6.15** A cartridge is considered clogged if a flow rate of 4 mL/min cannot be

achieved. If the tube clogs during sample loading, a second cartridge can be used for the sample and then extracts are combined. Alternatively, measure the amount of sample successfully extracted, and use that volume for the extraction constant. If this approach is used, then the surrogate and spike volumes must be corrected for the new initial volume. See Section 11 on how to calculate the actual surrogate and spike volumes.

- 10.6.16** As the sample level in the container drops, rinse the walls of the container with HPLC water. If a clip was used to keep the end of the line off of the bottom of the sample bottle and away from solids, lower it at this point in an attempt to extract the entire sample. If there is so much sediment that rinsing will cause the sediment to clog the cartridge, write an NCM stating the rinse could not be performed.
- 10.6.17** After all of the sample and the water used to rinse the container has gone through the line, close the valve and remove the line and the cap from the cartridge. If the valve was not closed before the cartridge went dry, rehydrate the packing as soon as possible with reagent water. It is important not to leave the cartridge packing dry, but do not leave any water remaining above the glass frit that sits on top of the column packing.
- 10.6.18** It is important not to let the cartridge go dry at this time, but to leave water in the cartridge.
- 10.6.19** After every sample and every QC sample has been loaded and all of the valves are closed and the caps removed, open all valves and pull a vacuum on all of the cartridges for 3 minutes to remove the remaining sample and to dry the cartridge. Care should be taken that the samples are only dried for 3 minutes.
- 10.6.20** Turn off the vacuum, close all of the valves, and remove the manifold lid. Rinse the needles on the underside of the manifold lid with HPLC grade methanol and wipe them with a clean lab tissue. Place it to the side on a clean lab tissue. Place the vial holder inside the manifold and place 8 mL HDPE vials that have been calibrated to 5 mL inside the manifold on top of the vial holder. Replace the manifold lid and be sure that each valve is positioned inside a vial.
- 10.6.21** Add 4 mL of HPLC grade methanol to each cartridge. Turn on the vacuum pump while the valves on the manifold are still closed, then quickly open and close each valve to create a vacuum in the cartridges. Turn off the vacuum pump open the manifold valve to break the vacuum in the manifold. Open the valves to allow the methanol to slowly drip gravimetrically (approximately one drop in 5 seconds.).
- 10.6.22** After the methanol has stopped dripping, reapply the vacuum to ensure that the last portion of methanol is collected. This is a very important step.
- 10.6.23** If two cartridges were used, transfer all extracts into one collection vial and

evaporate down to approximately 4 mL using a N-Evap. Continue to the next step.

- 10.6.24** Add HPLC grade water to the extract in the sample collection vial until the meniscus reaches the 5.0 mL mark.
- 10.6.25** The water sample extracts are ready for analysis. See SOP DV-LC-0012 for details on the analysis.
- 10.6.26** See Section 14.0 for proper disposal of all waste.

10.7 Soil Sample Extraction

Note: If samples are logged for prep method PFC_Leach and analytical method 8321A_HFPO_Du, do not follow the procedure described in 10.7. Instead, follow the procedure described in section 10.8.

- 10.7.1** Visually inspect soil samples for homogeneity.
- 10.7.2** Weigh a representative 10-11 gram amount of each soil into a 125-mL polypropylene wide-mouth bottle. Weigh additional sample amounts for the matrix spike and sample duplicate. Use baked Ottawa sand for the method blank and LCS sample matrix
- 10.7.3** Using a calibrated pipette, add 0.4 mL of the correct internal standard to every sample and every MS/MSD, duplicate, MB and LCS/LCSD sample. To determine the correct internal standard solution, check the analytical method logged and reference WI-DV-0009.
 - 10.7.3.1** If the sample is logged for analytical method LCMS_PFOA then the analytes of interest include PFOA and PFOS only and the "PFOA/S_Sur/IS" solution described in Section 7.13 should be used.
 - 10.7.3.2** If the sample is logged for analytical method PFC, then the analytes of interest include additional PFC compounds and the "PFC_Surr&IS", solution described in Section 7.14 should be used.
- NOTE:** The addition of all spikes and surrogates should be done immediately following a review by a 2nd analyst. See WI-DV-0009.
- 10.7.4** Using a calibrated pipette, add 0.4 mL of the correct spike solution to the MS/MSD samples and any LCS or LCSD. To determine the correct spike solution, check the analytical method logged and reference WI-DV-0009.
 - 10.7.4.1** If the sample is logged for analytical method LCMS_PFOA then the analytes of interest include PFOA and PFOS only and the

“PFOA/S_Spike” Solution described in Section 7.9.3 should be used.

10.7.4.2 If the sample is logged analytical method PFC, then the analytes of interest include additional PFC compounds and the “PFC-LCS-BR” solution described in Section 7.11 should be used.

10.7.5 Using a calibrated bottle top pump or a Class A graduated cylinder, add exactly 3 mL of 0.67 N NaOH described in Section 7.4 and allow the sample to soak for 30 minutes.

10.7.6 Using a calibrated bottle top pump or a Class A graduated cylinder, add exactly 10 mL of HPLC grade methanol to each field sample and QC sample.

10.7.7 Tumble each sample at room temperature for 24 hours.

NOTE: Make sure that tape is placed over the label to prevent it from being rubbed off.

10.7.8 Add 1 mL of the 2.4 M HCl solution described in Section 7.5 to all samples and gently mix. Measure the pH of the extraction solution with wide range pH paper. If the pH is greater than 7, add an additional 1 mL of 2.4 M HCl. Repeat the HCl additions until the pH measures less than 7. Note how much acid is added to each sample.

10.7.9 Using a calibrated pipette, or a Class A graduated cylinder, add the appropriate amount of HPLC grade methanol to adjust the extract solution to 20 mL. For samples that required only 1 mL of 2.4 M HCl solution in Section 10.7.8 above, 5.6 mL of HPLC grade methanol is needed to reach a final volume of 20 mL. For LCS and MS/MSD samples the final volume will be 20.4 mL.

NOTE: If more than 1 mL of HCl was added in Section 10.7.9 then add less methanol so that the final volume remains 20 mL, (20.4 mL for LCS and MS/MSD samples). For example, if it required 2 mL of HCl to achieve a pH less than 7, then only 4.6 mL of HPLC grade MeOH should be added.

10.7.10 Shake briefly to mix.

10.7.11 The samples may be centrifuged to help facilitate the filtration. Withdraw a 5-mL aliquot of the supernatant liquid and filter through a 0.45- μ m PVDF syringe filter into a labeled 10 mL HDPE vial.

10.7.12 The soil sample extracts are ready for analysis. See SOP DV-LC-0012 for details on the analysis.

10.7.13 See Section 14.0 for proper disposal of all waste.

10.8 Soil Sample Extraction for analytical method 8321A_HFPO_Du

Note: These samples are prepared with a final volume of 50 mL.

10.8.1 Visually inspect soil samples for homogeneity.

10.8.2 Weigh a representative 10-11 gram amount of each soil into a 125-mL polypropylene wide-mouth bottle. Weigh additional sample amounts for the matrix spike and sample duplicate. Use baked Ottawa sand for the method blank and LCS sample matrix.

10.8.3 Using a calibrated pipette, add 1.0 mL of HFPO I.S. (described in section 7.16) to every sample and every MS/MSD, duplicate, MB, and LCS/LCSD/LLCS sample.

NOTE: The addition of all spikes and surrogates should be done immediately following a review by a 2nd analyst. See WI-DV-0009.

10.8.4 Using a calibrated pipette, add 1.0 mL of HFPO Spike (described in section 7.17) to the MS/MSD samples and any LCS or LCSD. Add 0.1 mL of HFPO Spike to any LLCS.

10.8.5 Cap the bottles and allow the standards to settle into the sample matrix. Gently shake the bottles to mix the spike into the matrix.

10.8.6 Using a calibrated bottle top pump or a Class A graduated cylinder, add enough volume of the 5% NH₄OH solution described in section 7.7 to bring the extract volume to 45 mL. For example, add 43 mL to any LCS, MS, and add 44 mL to the MB, field samples, and LLCS.

10.8.7 Seal the bottles and vortex to completely mix the soil and the extraction solvent. Typically, 10-15 seconds on the vortex is sufficient, but depending on the sample matrix, some samples may require more time.

10.8.8 Tumble each sample at room temperature for 18-24 hours.

NOTE: Make sure that tape is placed over the label to prevent it from being rubbed off.

10.8.9 Add 5 mL of the 2% Formic Acid solution described in 7.8 to all samples and gently mix. This brings the volume to 50 mL.

10.8.10 Shake briefly to mix.

10.8.11 The samples may be centrifuged to help facilitate the filtration. Withdraw a 5-mL aliquot of the supernatant liquid and filter through a 0.45- μ m PVDF syringe filter into a labeled 10 mL HDPE vial.

10.8.12 The soil sample extracts are ready for analysis. See SOP DV-LC-0012 for details on the analysis.

10.8.13 See Section 14.0 for proper disposal of all waste.

10.9 Maintenance

Not applicable for this procedure.

10.10 Troubleshooting

When dealing with unusual sample matrices, consult QA or a supervisor.

11.0 Data Analysis and Calculations

Volume of Surrogate or Spike Extracted = $(V_{SA}) \times (V_E) \div (V_I)$

Where:

V_{SA} = Volume of Spike or Surrogate originally added.

V_E = Volume of Sample that was extracted through the cartridge

V_I = Volume of Sample that was originally spiked

Example: 0.1 mL of surrogate standard was added to a 253 mL sample. During the extraction, the cartridge clogged and only 233 mL of sample was actually extracted.

$$\begin{aligned}\text{Volume of Surrogate Extracted} &= 0.1 \text{ mL} \times 233 \text{ mL} \div 253 \text{ mL} \\ &= 0.092 \text{ mL}\end{aligned}$$

Therefore the initial volume on the benchsheet should be entered as 233 mL and the volume of surrogate should be entered as 0.092 mL.

12.0 Method Performance

12.1 Method Validation

Because this method has not been validated by an authoritative standards setting body, such as the U.S. EPA or ASTM, TestAmerica Denver conducted a series of method validation studies before writing this SOP. The validation studies were based on the guidelines of the U.S. EPA Pesticide Program. These studies are described in detail in the TestAmerica Denver documents "Method Validation Study for Analysis of Perfluorooctanoic Acid in Waters by High Performance Liquid Chromatography / Tandem Mass Spectrometry (HPLC/MS/MS)" and "Method

Validation Study for Analysis of Ammonium Perfluorooctanate in Soil Matrices by High Performance Liquid Chromatography / Mass Spectrometry (HPLC/MS/MS).”

- 12.2** 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. The MDL is determined according to the laboratory’s MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.3 Demonstration of Capabilities

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

- 12.3.1** Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.
- 12.3.2** Calculate the average recovery and standard deviation of the recovery for each analyte of interest.
- 12.3.3** 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 evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- 12.3.4** Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.
- 12.3.5** Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.4 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under supervision prior to approval of the IDOC. Documentation that a new analyst is performing under 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 DV-QA-0024.

13.0 Pollution Control

- 13.1 Solid phase extraction used for water samples greatly reduces the amount of solvent used compared to liquid/liquid extraction.
- 13.2 Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

- 14.1 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 procedure, the policies in the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."
- 14.2 The following waste streams are produced when this method is carried out:
 - 14.2.1 Methanol waste – Flammable Solvent (C)
 - 14.2.2 Water Samples, post extraction and all other aqueous waste generated by this procedure is collected and turned into the Waste Coordinator for incineration under waste stream PFOA.
 - 14.2.3 Soil Samples, post extraction and all other solid waste generated by this procedure such as disposable pipette tips and extraction bottles are collected and turned into the Waste Coordinator for incineration under waste stream PFOA.
 - 14.2.4 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

NOTE: Radioactive and potentially radioactive or mixed waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

Method 3535A, Solid-Phase Extraction (SPE), Revision 1, February 2007

16.0 Method Modifications:

The SPE procedure is modified from SW-846 Method 3535A in order to achieve the optimum recovery for the analytes of interest.

17.0 Tables

- Table 1: Perfluorinated Hydrocarbons (PFCs)
- Table 2: Isotopically Labeled PFCs

Table 3: Surrogate Compounds

18.0 Revision History

18.1 Revision 9, dated 8 December 2017

- Changed all references to PFC-LCS to the new standard name, PFC-LCS-BR.
- Added section 7.7 to include 5% Ammonium Hydroxide reagent; renumbered subsequent entries in section 7.
- Added 7.16 and 7.17 to include HFPO-DA standards.
- Added detail to 10.5.1 to include HFPO-DA.
- Added 10.5.8.3 and 10.5.9.3 (and renumbered subsequent sections) to include standards used for HFPO-DA.
- Added Note to section 10.7 to redirect to 10.8 for HFPO-DA soils.
- Added section 10.8 to outline procedure developed for extracting HFPO-DA from soils.

18.2 Revision 8, dated 31 October 2016

- Added initial paragraph to section 3.0 to reference the QAM for general analytical and QA/QC terms
- Added initial paragraph to section 6.0 regarding the documentation of support equipment IDs
- Added section 6.3 on Software and Hardware
- Updated sections 6.2.1, 7.6, 7.9, 7.11.1, 7.12.1, 7.13.1, 7.14.1, 10.3.12, 10.3.20, 10.4.10, 10.4.21, 10.5.6, 10.5.9 to reflect the change from using LCMS grade methanol to HPLC grade Methanol. Per the company, HPLC grade is now clean enough to use for preparation and analysis.
- Removed section 7.2 regarding LCMS grade MeOH used in the making of standards, conditioning of SPE cartridges, the extraction of water samples for FOSA and the extraction of soil samples.
- Updated section 7.1 with information regarding HPLC grade MeOH used in the making of standards, conditioning of SPE cartridges, the extraction of water samples for FOSA, and the extraction of soil samples.
- Updated section 9.1 and its subsections to reflect current practices and consistent verbiage
- Removed "At least" from section 9.4 to reflect that one MB is performed for each batch
- Added numbering to sections 9.6.1 and 9.6.2
- Added LCS/LCSD requirements when no MS/MSD to sections 9.5, 9.6.2, 10.5.7, 10.6.4.
- Added section 10.3 comment regarding the rotation of glassware and positions
- Added section 10.4 regarding the documentation of support equipment IDs

18.3 Revision 7, dated 31 October 2015

- Removed Confidentiality Restriction Note boxes

- Updated Sections 12.2 and 12.3 to reflect consistent information as provided in other SOPs.
- Section 6.1 was revised to include a centrifuge in the equipment list.
- Added instructions to the solid phase extraction procedure to cap and shake water samples after the addition of the surrogate and spike standards.
- Added instructions to the solid phase extraction procedure to use centrifuge to separate solids from the sample to prevent the cartridge from clogging. Also instructed analysts to write an NCM if sediment prevents them from rinsing the sample container.
- Revised the solid phase procedure to clarify that it is important to re-hydrate the cartridge packing as soon as possible if the cartridge goes dry.
- Revised the pre-conditioning of the FOSA cartridge to be 24 mL instead of 48 mL of water to bring the procedure in line with other SPE methods.

18.4 Revision 6, dated 13 October 2014

- Revised Section 6.2.4 and 10.3.11 to reflect current cartridge in use and added "or equivalent" to enable laboratory obtain cartridges from another vendor or change the cartridge to obtain equivalent performance.
- Updated Section 8 to revise HT for water to reflect validation study performed by TestAmerica Denver and to be consistent with Section 8 in the analytical SOP, DV-LC-0012.
- Added new section 12.2 to address MDLs/verification of MDLs.
- Replaced $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ with $0\text{-}6^{\circ}\text{C}$ for consistency with current EPA practice and laboratory control limits on refrigerator temperatures.
- Formatting and editorial changes throughout.

18.5 Revision 5, Dated 04 March 2014

- The procedure was revised to remove the 3 hour sonication step in the soil extraction. A new MDL study and IDOC were performed prior to the change.
- Troubleshooting and Maintenance Sections were added per DoD QSM 5.0.
- Section 9.1 was revised to state the procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.
- Sections 9.4, 9.5, 9.6, 9.7, and 9.8 were revised to remove acceptance criteria and corrective actions. This information can be found in the analytical SOP.
- Section 10.1 was revised to clarify that any deviations from this procedure discovered after the work has been performed must be documented in an NCM.
- Section 10.4.2 was revised to give a range for the initial sample mass.
- Section 10.4.11 was revised to place the centrifuge step before the instructions to withdraw the supernatant.

18.6 Revision 4, Dated December 10, 2013

- Confidential information included

18.7 Revision 3, Dated March 4, 2013

- Annual Technical Review
- Section 2.3 was revised to better explain that the soil extracts are brought up to final volume with methanol.
- Section 10.2.18 was revised to better explain that the cartridge packing cannot be allowed to go dry, but excess water should not be left in the cartridge.
- Section 10.2.21 was revised to give guidance on how to avoid cross-contamination during the rinsing of the manifold lid.
- Section 10.4.5 was removed as the 0.4 mL of IS and 0.4 mL of spike solution readily absorbs into the sample and therefore capping and shaking was not necessary.
- Section 10.4.6 and 10.4.7 (now 10.4.5 and 10.4.6) were revised to match current practice of using a calibrated bottle-top pump instead of a mechanical pipette to add the NaOH and the MeOH.

18.8 Revision 2.1, Dated January 31, 2012

- Removed references to method "8321_PFC_Du" from the soil extraction procedure as the extraction required is no longer per this procedure, but per a client specific QAS.
- Section 2.3 was corrected to state that soil samples are adjusted to a pH less than or equal to 7.
- Section 6.1 was corrected to state that the balance is capable of measuring $\pm 0.1\text{g}$.
- Section 6.2 was corrected to state that the Waters Oasis WAX cartridges are 150 mg.
- Sections 7.6, 7.7, and 7.8 were revised to instruct analysts to add acid and base to water instead of adding water to the acids and base.
- Updated Section 9.1 and 10.1 to reflect the current NCM process.
- Added clarification to Sections 10.2.17 and 10.3.17 on how to calculate the volume of surrogate and spike extracted when a cartridge clogs. Added Section 11 to include the formula required to do the calculation.

18.9 Revision 2, dated January 21, 2011

- The procedure was revised to disallow the use of glass volumetrics in the aliquotting of samples. This was done to prevent loss of target analytes as the target analytes are known to adhere to glass.
- The procedure was revised to change the final extract volume for soil extracts from 50 mL to 20 mL. The volume of spike, internal standards, and surrogate standards used in the extractions were changed to maintain the spike concentration in the extract.
- The internal standard used to quantitate the concentration of FOSA has been changed from MeFOSA to 13C8 FOSA.
- The extraction procedure in Section 10.3 for the extraction of FOSA was revised extensively. This was done to compensate for matrix issues arising from the high pH required in the old procedure.

Earlier revision histories have been archived and are available upon request.

Table 1 – Perfluorinated Hydrocarbons (PFCs)

NAME	ABBREVIATION
Perfluorodecane sulfonate	PFDS
Perfluorohexane sulfonate	PFHxS
Perfluorobutyric acid	PFBA
Perfluoropentanoic acid	PFPA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Perfluorotridecanoic acid	PFTriA
Perfluorotetradecanoic acid	PFTeA
Perfluorobutane sulfonate	PFBS
Perfluorooctanoic sulfonate	PFOS
Perfluorooctanoic acid	PFOA
Perfluorooctane sulfonamide	FOSA

Table 2 – Isotopically Labeled PFCs

NAME
13C4 PFOA
13C4 PFOS
13C4 PFBA
13C4 PFHxA
18O2 PFHxA
13C5 PFNA
13C2 PFDA
13C2 PFUnA
13C2 PFDoA
13C8 FOSA

Table 3 – Surrogate Compounds

NAME
13C8 PFOA
13C8 PFOS