3M EHS Laboratory

Method

Solvent Extraction and Gradient or Isocratic LC/MS/MS Analysis of Soils for C4-C12 Perfluorinated Carboxylic Acids, and Perfluorobutane Sulfonate, Perfluorohexane Sulfonate, Perfluorooctane Sulfonate and Perfluorooctane Sulfonamide (FOSA): Quantification Using Stable Isotope Labeled Internal Standards

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Quality Assurance

1 Scope and Application

Described herein is a performance-based LC/MS/MS method that provides instruction for the extraction and analysis of C4 to C12 perfluorinated carboxylic acids (PFCAs) and C4, C6 and C8 perfluorinated sulfonic acids (PFSAs), and perfluorooctane sulfonamide (FOSA) from soils and sediments.[1] The method was developed for extraction of an accurately weighed 1 cubic centimeter (cc) volume of sample. This method does not describe sieving or other sample clean-up prior to extraction/analysis, therefore, samples having rocks, twigs or other debris are precluded from this method and may require cleanup by sieving or pulverizing prior to soil aliquot removal from bulk samples. This method applies to more homogenous soils consistent with sand, sandy gravel (low rock content), clay, loams, sediments, etc. Target analyte concentrations in samples are determined from calibration curves constructed with data from the analysis of a set of extracted matrix-matched calibration standards prepared with laboratory control soils, or other control matrix as appropriate, or by solvent calibration. This method may be extended to other matrices and test systems (e.g. sludge or sediment) provided the data quality objectives defined herein are met.

Application of this method to additional perfluoroalkyl substances (PFAS) must meet the same quality control acceptance criteria described herein. The method may also be applied to other matrices such as dust, debris and sludge.

If available, certified linear isomer reference substances should be applied for preparation of calibration standards and quality controls (QCs). Alternatively, certified technical grade reference materials may be used for calibration and/or QC preparations. The specific reference materials and their use should be documented in the study specific GPO.

The isocratic HPLC/MS/MS aspect of this method was validated as project E09-0119. The gradient HPLC/MS/MS aspect of this method was validated as project E10-0020. Method validations include evaluations for accuracy, precision, specificity, selectivity, matrix-matched calibration, solvent calibration, limits of quantitation (LOQs), dilution accuracy, ruggedness, absolute recovery (matrix effects), carry over, and stability of refrigerated soil samples and ambient stored soil extracts.

Table 1. Representative Target Analytes

Acronym	*Analyte*	*CAS #*
Perfluorinated Carboxylates (PFCAs)		
PFBA (C4 Acid)	Perfluorobutanoic acid	375-22-4
PFPeA (C5 Acid)	Perfluoropentanoic acid	2706-90-3
PFHxA (C6 Acid)	Perfluorohexanoic acid	307-24-4
PFHpA (C7 Acid)	Perfluoroheptanoic acid	375-85-9
PFOA (C8 Acid)	Perfluorooctanoic acid	335-67-1
PFNA (C9 Acid)	Perfluorononanoic acid	375-95-1
PFDA (C10 Acid)	Perfluorodecanoic acid	335-76-2
PFUnA (C11 Acid)	Perfluoroundecanoic acid	2058-94-8
PFDoA (C12 Acid)	Perfluorododecanoic acid	307-55-1
Perfluorinated Sulfonates (PFSAs)		
PFBS (C4 Sulfonate)	Perfluorobutane sulfonic acid	375-73-5

[1] This method is supported by validation with internal standard calibration based on LCSs prepared and analyzed during method validations as 3M studies E09-0119 (isocratic analysis) and E10-0020 (gradient analysis). The PFBA (C4 PFCA) and PFPeA (C5 PFCA) were added based on results from 3M study E13-0088.

Table 1. Representative Target Analytes		
Acronym	***Analyte***	***CAS #***
PFHS (C6 Sulfonate)	Perfluorohexane sulfonic acid	355-46-4
PFOS (C8 Sulfonate)	Perfluorooctane sulfonic acid	1763-23-1
FOSA (C8 Sulfonamide)	Perfluorooctane sulfonamide	754-91-6

Method Flexibility – This is a performance-based method that may be generally applied to the determination of PFAS in any solid environmental matrix (i.e. soil, sediment, sludge, compost, etc.) when analysis batch quality control (QC) criteria are met2. Each set of samples are prepared in an analytical batch in parallel with calibration standards, LCSs, blanks, and continuing calibration check standards which are analyzed on the same instrument during a period that begins and ends with the analysis of continuing calibration check standards. The laboratory is permitted to modify the LC column, mobile phase composition, LC conditions, and MS/MS conditions. Method modifications should be considered to improve method performance or to meet data quality objectives for the study. In all cases where method modifications are implemented, the batch analytical QCs defined herein must be completed and pass QC acceptance criteria if the data from the analytical batch are to be reported.

2 Method Summary

This analytical method criteria are based on validation data collected as study E10-0020, and also based on additional results from laboratory control matrix spike (LCS) and laboratory matrix spike (LMS) samples evaluated in numerous studies for analysis of field samples. This document describes the procedure for the extraction and quantitation of PFSAs and PFCAs in soils. In brief, a 1 cubic centimeter (1 cc, 1 mL) aliquot is taken from a bulk sample and transferred to a 15-mL polypropylene centrifuge tube using a fixed volume 1 cc plastic spoon. The aliquot's mass is then accurately determined minimally to 0.001 grams. Stable isotope labeled internal standards (ISs) are added to the soil and then 8-mL of a 4:1 (v/v) acetonitrile-water extraction solvent is added. The mixture is briefly mixed and then sonicated in a sonicating water bath for approximately 1 hour. After sonication, the mixture is centrifuged at approximately 3000 rpm for 5-10 minutes to pellet out solids. An aliquot of the clarified supernatant is then transferred to an autovial for analysis by high performance liquid chromatography tandem mass spectrometry (LC/MS/MS). Quantitation is performed using matrix-match calibration using a standard control soil and is conducted by internal standard method. The specified quality control criteria for this method are defined in section 10.

3 Definitions

3.1 Reagent Grade Water

Reagent grade water is defined as water with no significant levels of target analyte or other impurities present at or above a level that affects the LLOQ objectives of the study. A Millipore Milli-Q™ water purification system, or equivalent purification system, can provide adequately pure reagent water used for this method.

[2] Guidance for establishing method QC Criteria based on a.) FDA May 2001, "Guidance for Industry, Bioanalytical Method Validation", b.) EPA Method 537, and c.) European Commission: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-registration Data Requirements for Annex II (Part A, section 4) and Annex III (Part A, section 5) of Directive 91/414, SANCO/3029/99 rev. 4 (11/07/00).

3.2 Method Blank

Method blanks are prepared from an aliquot of control matrix that is treated exactly like a laboratory sample including exposure to all glassware, equipment, solvents, and reagents used with other laboratory samples. Two types of method blanks are typically prepared: (1) control soil matrix alone, and (2) control soil matrix with IS. Typically, two or more method blanks are prepared for each type. The method blanks with IS are used to determine LLOQs if a calibration blank is not created.

3.3 Bulk Sample

A bulk sample is the soil sample collected in the field and provided to the laboratory for analysis, typically contained within a 250 mL HDPE bottle. This sample may contain water, and should be homogenized by thoroughly shaking and/or stirring the sample contents prior to taking the analytical sample.

3.4 Analytical Sample

An analytical sample is an aliquot removed from the bulk soil sample, intended to represent the original source material and prepared for analysis.

3.5 Analytical Sample Duplicate (Laboratory Duplicate, LDS or Lab Dup)

A second analytical sample is an aliquot removed from the bulk soil identical to the primary analytical sample, intended to represent the original source material and is extracted and analyzed. Results from the primary sample and duplicate sample provide a measure of the reproducibility of the analytical result. The reproducibility is typically represented by the relative percent difference (RPD) of the two results, and may be as high as 50% for more heterogeneous soil types (i.e. sandy gravel or gravel), or less than 20% for more homogenous soil types (i.e. sand, clay). The data acceptance criteria for duplicate sample RPDs will be defined in the General Project Outline (GPO) or test protocol and based on the anticipated soil types from the field.

3.6 Internal Standard (IS)

Stable isotope labeled internal standards (ISs) are available from several commercial suppliers, such as Wellington Laboratories. The following list of ISs is not intended to be exhaustive, and new stable isotope labeled internal standards frequently become available and may be used, as appropriate. Examples of appropriate ISs for this method are listed in Table 2.

Table 2. Stable Isotope Labeled Internal Standards

Chemical Name	*Synonym or Acronym*	*Chemical Formula*	*Analytical Use*
$^{13}C_4$-Perfluorobutanoic acid	[1,2,3,4-$^{13}C_4$] PFBA	$CF_3(CF_2)_3(^{13}CF_2)^{13}COOH$	IS for PFBA
$^{13}C_5$-Perfluroopentanoic acid	[1,2,3,4,5-$^{13}C_5$] PFPeA	$CF_3(CF_2)_3(^{13}CF_2)^{13}COOH$	IS for PFPeA
$^{13}C_2$-Perfluorohexanoic acid	[1,2 -$^{13}C_2$]-PFHxA	$CF_3(CF_2)_3(^{13}CF_2)^{13}COOH$	IS for PFHxA
$^{13}C_4$-Perfluoroheptanoic acid	[$^{13}C_4$]-PFHpA	$^{13}CF_3(^{13}CF_2)_5\ ^{13}COOH$	IS for PFHpA
$^{13}C_8$-Perfluorooctanoic acid	[$^{13}C_8$]-PFOA	$^{13}CF_3(^{13}CF_2)_6\ ^{13}COOH$	IS for PFOA
$^{13}C_9$-Perfluorononanoic acid	[$^{13}C_9$]-PFNA	$^{13}CF_3(^{13}CF_2)_7{}^{13}COOH$	IS for PFNA
$^{13}C_6$-Perfluorodecanoic acid	[$^{13}C_6$]-PFDA	$CF_3(CF_2)_3(^{13}CF_2)_5{}^{13}COOH$	IS for PFDA
$^{13}C_7$-Perfluoroundecanoic acid	[1,2,3,4,5,6,7 -$^{13}C_7$]-PFUnA	$CF_3(CF_2)_3(^{13}CF_2)_6{}^{13}COOH$	IS for PFUnA
$^{13}C_2$-Perfluorododecanoic acid	[1,2 -$^{13}C_2$]-PFDoA	$CF_3(CF_2)_9(^{13}CF_2)^{13}COOH$	IS for PFDoA
$^{18}O_2$- Perfluorobutane sulfonate	[$^{18}O_2$]-PFBS	$[C_4F_9S^{18}O_2O]^-\ NH_4^+$	IS for PFBS
$^{13}C_3$- Perfluorohexane sulfonate	[1,2,3 -$^{13}C_3$]-PFHS	$[C_3{}^{13}C_3F_{13}SO_3]^-\ Na^+$	IS for PFHS
$^{13}C_8$-Perfluorooctane sulfonate	[$^{13}C_8$]-PFOS	$[^{13}C_8F_{17}SO_3]^-\ Na^+$	IS for PFOS
$^{13}C_8$-Perfluorooctanesulfonamide	[$^{13}C_8$] FOSA	$[^{13}C_8F_{17}SO_2NH_2]$	IS for FOSA

As other stable isotope labeled potential internal standards are made commercially available, they may be used in substitution for one or more of those listed.

3.7 Calibration Standard Spiking Solutions

A solution of several analytes prepared in the laboratory from laboratory-prepared stock solutions or commercially provided stock solutions. These may be diluted as needed to prepare calibration standards and other required analyte solutions.

3.8 Matrix-Matched Extracted Calibration Standards

A solution prepared by spiking a known volume of the calibration standard spiking solution, including analytes and IS, into a predetermined amount of soil and analyzed according to this method. Matrix-matched calibration standards are used to calibrate the instrument response with respect to analyte concentration in matrix samples.

3.9 Unextracted (solvent) calibration

A solution prepared by spiking a known volume of calibration standard spiking solution, including analytes and IS into a predetermined amount of extraction solvent and analyzed according to this method. Solvent calibration standards are used to calibrate the instrument response with respect to analyte concentration in the extraction solvent. This standard is used to achieve a lower limit of quantitation.

3.10 Calibration blank

A calibration blank is a blank prepared at the same time as the calibration standards using the same matrix (i.e. soil or acetonitrile).

3.11 Limits of Quantitation

The lower limit of quantitation (LLOQ) are analytical batch specific and analyte specific and is defined as the lowest non-zero standard in the calibration curve that meets method (100 +35%) or study specified acceptance criteria, and is typically defined by the lowest level standard with a target

analyte peak response that is at least 2-times the analyte peak response of a method blank and still meets the specified limits of accuracy. The upper limit of quantitation (ULOQ) is the highest concentration standard reliably quantified within the specified limits of accuracy for the method (100 +30%).

3.12 Laboratory Control Spike (LCS)

An aliquot of control matrix to which known quantities of the target analytes and ISs are added in the laboratory at the time when samples are aliquoted. At least three levels in triplicate are included, one generally at the low end of the calibration curve and one near the mid-range and the upper end of the curve. The LCSs are analyzed exactly like a laboratory sample as a measure of the method accuracy, precision, and uncertainty. LCSs should be prepared each day with samples.

The LCS results are typically evaluated to determine analytical method accuracy (average LCS recovery, all levels) and analytical method uncertainty (per ETS-12-012). The LCSs are also evaluated to determine the method precision as percent relative standard deviation (RSD).

3.13 Trip Blank (a.k.a. Travel Blank)

A quantity of sufficiently clean control soil matrix placed in a sample bottle in the laboratory and that travels to the site with empty sample collection bottles, and then returns with the samples, and is treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of a Trip Blanks is to ensure that contamination of the samples did not occur during shipment and/or storage.

3.14 Laboratory Matrix Spike (LMS)

A LMS is an aliquot of a sample to which known quantities of target analytes are added in the laboratory and used to evaluate sample-specific analyte recovery. The LMS is extracted and analyzed the same as a laboratory sample and the spike recovery result used to determine whether the sample matrix affects the analytical result for the sample.

3.15 Analytical Batch

A comprehensive set of samples, LMSs, LCSs, Blanks and Calibration Standards that are prepared together, typically on the same day, and analyzed together as an analytical run (a.k.a. batch or run). The samples and associated QCs as LMSs, LCSs and different blanks are then evaluated together as a whole to ensure the sample results from that batch meet data quality objectives for reporting.

4 Warnings and Cautions

4.1 Health and Safety Warnings

All personnel performing these procedures are required to know the appropriate protective equipment to wear and procedures to follow during extraction and analysis, including the following: use of protective gloves, eye protection, and appropriate clothing/lab coats and working within fume hoods with unknown sample matrices, solvents, chemicals and instrumentation, when applicable. For potential hazard information refer to material safety data sheets, packing material, the 3M EHS Laboratory's Chemical Hazard Review, the study/project lead and the 3M Guide to Laboratory Practices, as appropriate.

The shipping and receipt of regulated soils is covered under the laboratory's USDA soils permit, and knowledge of potentially regulated soil from certain regions of the U.S., and proper soil sample shipping & handling is required. The pertinent soil shipping and receipt procedures can be found in SOP ETS-4-033.

4.2 Cautions

The analyst must be familiar with the laboratory equipment and potential hazards including, but not limited to, the use of balances, centrifuges, flammable and/or toxic solvents, ovens, pressurized gases and static and high voltage sources. Refer to the appropriate equipment SOPs and operator manuals for additional information and cautions.

5 Interference

To minimize potential interference from instrument or Labware contamination with perfluorinated analytes, polytetrafluoroethylene (PTFE, Teflon®) should be avoided for sample storage and replaced with non-PTFE component, when possible, if it is part of instrumentation that contacts the sample or extract during analysis.

Co-extracted matrix components may also enhance or suppress the measured analyte signal in the mass spectrometer, therefore, the evaluation of method quantitative accuracy relies heavily upon LMS results.

6 Instrumentation, Supplies and Materials

The following instrumentation, supplies, and materials are used while performing this method. Other equivalent instrumentation, supplies, and materials may be used in place of those listed. Newer models of the same instrumentation are all considered equivalent, or better.

6.1 Instrumentation

Analytical Balance, (for accurate determination to 0.001 g, or lower)

Agilent HPLC 1100, or equivalent:

Pump: Quaternary Pump, Agilent®, Model G1311A; or Binary Pump, Agilent®, Model 1312

Solvent Degasser, Agilent®, Model G1322A

Autosampler, Agilent®, Model G1313A, or Thermostat Controlled Autosampler, Agilent®, Model G1329A

Column Compartment (Temperature Controlled), Agilent®, Model G1316A

Controller, Hand Held, Agilent®, Model # G1323A

Applied Biosystems MDS SCIEX API 4000 Triple Quadrapole Mass Spectrometer, or equivalent

SCIEX Turbo Ion Spray Liquid Introduction Interface

Other instrumentation as needed, document as appropriate

6.2 Supplies and Materials

1 cubic centimeter (1 cc, 1 mL) fixed volume plastic sampling spoons (Science Ware™)

Hamilton gas tight syringes (capable of dispensing at least 50 µL)

Class A volumetric flasks

Micropipettes, Eppendorf™ or equivalent, and disposable micropipette tips

Thermo Fischer Scientific Betasil C18, 2.1 x 100 mm, 5 µm particle size

Thermo Fischer Scientific Prism™ RP 2x50 mm, 5 µm particle size

HPLC autosampler vials capable of containing approximately 1-2 mL of extract

Waters Corporation, Oasis HLB Online Column, 3 x 20 mm 25 um particle size.

Disposable centrifuge tubes, polypropylene, various sizes (i.e. 15 mL and 50 mL)

Other supplies and materials as needed, document as appropriate

Various glass type-A volumetric flasks

Various glass pipettes

Other supplies and materials may be required that are not listed.

Soil aliquots may be pre-weighed (i.e. the day before) and stored sealed at room temperature until time of extraction.

Drying oven, capable of holding at between 100°C and 115°C; for percent moisture determinations of samples.

Thermometer, digital or equivalent.

7 Reagents and Standards

Reagent grade water (Milli-Q™, or equivalent)

Methanol, HPLC grade or equivalent.

Acetonitrile, HPLC grade or equivalent

Ammonium Acetate (99%, or better), ACS grade

Acetic Acid (glacial)

C4 to C12 perfluorinated carboxylic acids reference substances, or equivalent salts

C4, C6 and C8 perfluorinated alkyl sulfonic acid reference substances, or equivalent salts

Stable isotope labeled C4 to C12 PFCAs, PFSAs and FOSA references, as necessary for ISs.

8 Analytical Procedures

The composition of soils, sediments, sludge, etc. are typically not homogenous and target analytes may be distributed heterogeneously throughout the sample. This can result in higher RSDs or RPDs between replicate results for such samples, hence a typically increased acceptance criterion for RSDs and RPDs for these types of samples when analyzed in multiple replicates. It is recommended to homogenize such samples as much as possible without risking contamination of the sample. Ideally, the soil, sediment or sludge samples are homogenized in the field at the time of collection, but this is outside the control of the laboratory. Additional homogenization in the laboratory can be as simple as vigorously shaking the sample in a sample bottle to break up sample clumps or to re-distribute any settled water phases (in the case of wet soils, or sediment and sludge samples). Observations of persistent clumping and heterogeneous soil should be noted during sample preparation so as to correlate these observations with any poor RSDs and RPDs for those samples. Issues with heterogeneity may be averted by using a larger sample volume for preparation, with appropriate adjustment for the extraction solution volume used. For example, a 5 cc aliquot of soil may be taken and extracted with 40 mL of extraction solvent.

Note: Surrogates must not be used for this method. Validation, E10-0020, results demonstrated that surrogates were not an indication of specific target analyte recoveries.

8.1 Sample and Extract Storage Stability

Samples should be analyzed within 2 weeks of being received at the laboratory to ensure full recovery of analytes, especially FOSA. If deviation of this procedure must occur then control soil must be spiked with analytes investigated on the day the soils are received and be extracted at the same time as the samples. All soil samples must be stored refrigerated. Extracts are stable for 2 weeks. All extracted soils must be stored refrigerated and analyzed within 2 weeks of extraction.

8.2 Sample Preparation

Other weights or volumes than the ones provided here may be used if adequate QC is performed and a 1 mL (1 cc) sample to 8 mL of extraction solvent ratio (1:8, v/v) is maintained.

Homogenize the bulk sample by thoroughly shaking and/or stirring the sample contents prior to taking the analytical sample. Tare a 15-mL conical centrifuge tube on a balance capable of accurate measurement to 0.0001 g. Carefully remove a 1 cubic centimeter (1 cc, 1 mL) aliquot of sample from the bulk sample using a 1 cc fixed volume disposable plastic spoon (be sure to level the top off so that it is flat and even on the sampling spoon). Transfer the aliquot of soil sample to the previously tared 15 mL conical tube. Determine and record the accurate weight of the sample. Sample replicates (duplicates, triplicates, etc.) will be prepared by weighing out a separate aliquot(s) of bulk sample for each.

Spike the sample aliquots with an appropriate calibration standard solution and internal standard solution.

Add 8 mL of a 4:1 (v/v) acetonitrile-water extraction solution and briefly shake or vortex the sample.

Place the sample in a sonicating water bath (approximately 20-30 °C) for approximately 1 hour.

Centrifuge the sample solution at a setting of 3000 RPM for 5-10 minutes.

All sample preparation solutions used, and any special observations, should be recorded appropriately in the preparation record.

8.3 Calibration Standard Spiking Solutions

Spiking solutions are prepared in organic solvent (methanol, ethanol, acetonitrile, etc.) and are used to add known quantities of target analytes and ISs into predetermined amounts of a control matrix or extraction solvent when preparing calibration standards for analysis. Spiking solutions for IS prepared at nominal 50 ng/mL for each IS substance using prepared stock solutions or commercially provided mixed stock solutions. Target analytes for spiking calibration standards are prepared in organic solvent at nominal concentrations of 10 ng/mL, 100 ng/mL and 1000 ng/mL for each, and can be from laboratory-prepared stock solutions or commercially provided stock solutions.

Due to potential acid-catalyzed esterification of PFCAs by reaction with hydrocarbon alcohols (i.e. methanol or ethanol) it is important to prepare stock solutions of PFCAs in acetonitrile or to treat them with small quantities of base (i.e. ammonium hydroxide). The analyst should review the certificate of analysis for each reference standard before proceeding to use the materials to determine purity and salt correction factors and expiration date. When available, certified commercially provided linear isomer reference materials for all target analytes should be used for calibration during this method, excluding study-specific circumstances where mixed linear and branched isomer reference materials (technical grade materials) are desired for calibration. Alternatively, certified technical grade reference materials consisting of mixed linear and branched isomers may be applied provided that LCSs made from linear isomer and LCSs from linear + branched isomer reference materials are included to demonstrate the accurate quantitation of both types of material.

8.4 Matrix-Matched Extracted Calibration Standards

Matrix-matched extracted calibration standards (containing variable concentrations of target analytes are prepared by spiking variable known quantities of target analytes into 1 cc aliquots of a standard reference soil, or other matrix, followed by addition of a fixed quantity of internal standard to each. The spiked matrix is then extracted as described herein. For practical purposes and ease of reporting, it will be assumed that all standard reference soil aliquots used for calibration are 1 gram per cubic centimeter if sufficiently devoid of target analytes.

Analytical results (analyte/IS ratio) from calibration standards are plotted to construct the calibration curve, and are then fitted by linear or quadratic regression, with 1/x or 1/x2 weighting, as needed. The final calibration curve must consist of at least six calibration points. The determined analyte/IS peak area ratio for each analyte for sample extracts is then correlated with the curve regression equation for determining unknown concentrations of target analyte in samples. Table 3 shows an example of a calibration standard set preparation.

Table 3. Example of Matrix-Match Extracted Calibration Standards

Sample Description	*Weight of Standard Soil Used for Extraction (g)*	*IS Spike Solution Volume (µL)*	*IS Spike Sol. Conc. (ng/mL; ppb)*	*IS Soil Spike Level (ng/g)*	*Target Analyte Spike Solution Volume (µL)*	*Target Analyte Spike Solution Conc. (ng/mL; ppb)*	*Target Analyte Calibration Standard Level (ng/g)*
Extracted Cal. Curve Point 1	1.0	100	50	5	10	10.0	0.100
Extracted Cal. Curve Point 2	1.0	100	50	5	25	10.0	0.250
Extracted Cal. Curve Point 3	1.0	100	50	5	50	10.0	0.500
Extracted Cal. Curve Point 4	1.0	100	50	5	100	10.0	1.00
Extracted Cal. Curve Point 5	1.0	100	50	5	25	100	2.50
Extracted Cal. Curve Point 6	1.0	100	50	5	50	100	5.00
Extracted Cal. Curve Point 7	1.0	100	50	5	100	100	10.0
Extracted Cal. Curve Point 8	1.0	100	50	5	25	1000	25.0
Extracted Cal. Curve Point 9	1.0	100	50	5	50	1000	50.0
Extracted Cal. Curve Point 10	1.0	100	50	5	100	1000	100

Calibration levels and spike solution concentrations shown are nominal. Additional curve points may be made by alternative dilution schemes for target analytes, as deemed necessary.

The number of calibration standards, spike volumes, and spike concentrations may be adjusted accordingly to meet the needs of the project and for preparation feasibility (i.e. when limited by quantity of available soil, available standards, limit of quantitation, etc.) The concentrations shown in the table above will usually suffice for analysis of most soils. Alternative spike solution concentrations may be used provided the spike volumes are adjusted appropriately to accommodate final calibration standard levels.

8.5 Unextracted (solvent) calibration

If matrix-matched extracted calibration is not possible, or not desired, then solvent calibration standards prepared in extraction solution with the appropriate reference target analytes at the appropriate concentrations may be used; prepared the same as matrix calibration standards, but without soil matrix, and using the same fixed concentration of IS as the samples.

8.6 Calibration blank

A calibration blank is a blank prepared at the same time, and way, as the calibration standards using the same matrix (i.e. soil or acetonitrile). The blank must contain IS to be used to determine LLOQs.

8.7 Laboratory Control Spike (LCS)

An LCS is prepared by using control soil matrix, adding known quantities of the target analytes, extracting and analyzing the same as samples. Typically, the LCS control matrix is the same or like that used to prepare the extracted soil matrix calibration standards. If not, then a set of method blanks should be prepared for the LCSs to evaluate for endogenous target analyte in the control matrix used for LCSs, and LCS results corrected for endogenous background levels. It is recommended that LCSs be prepared at levels that closely represent the anticipated concentration range of target analytes in samples. Typically, LCSs are prepared at three levels (low, mid and high relative to the calibration range), each level is typically prepared in triplicate. The LCS levels may be prepared at nominal 3 to 5-times the targeted LLOQ (low-LCS), a mid-level prepared near the geometric mean of the calibration range (mid-LCS), and a higher level at nominal 70-80% of the ULOQ (high-LCS). Typically, when samples require dilution and reanalysis, a set of diluted high-level LCSs are included with that analytical batch to evaluate dilution accuracy and precision.

The actual fortified levels of LCSs should be defined in the study GPO, and when not, the above defined nominal levels are recommended as a general guide.

At a minimum, one level of LCS should be included in each analytical batch, each level should be prepared in triplicate

8.8 Trip Blank (a.k.a. Travel Blank)

A trip blank is created before samples are collected and all preparation and shipping is properly documented. A set quantity of sufficiently clean control soil matrix is placed in a sample bottle in the laboratory and that travels to the site with empty sample collection bottles, and then returns with the samples, and is treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures.

8.9 Laboratory Matrix Spike (LMS)

A LMS is prepare by taking an aliquot of a sample and spiking known quantities of target analytes to evaluate sample-specific analyte recovery. The LMS is extracted and analyzed the same as a laboratory sample and the spike recovery result used to determine whether the sample matrix affects the analytical result for the sample. The determined endogenous concentration of analytes in the sample matrix must be determined in a separate aliquot, and measured values in the LMS corrected for the endogenous concentrations during spike recovery calculation. Because this method is performance based, LMSs are required to be prepared. Typically for soils, the appropriate fortified level most representative of the endogenous sample level for evaluating LMS recovery should between 0.5-times and 20-times the endogenous level. However, exceptions to this can be made and are study specific and the typical LMS acceptable fortification level range may be tightened or widened accordingly to accommodate the anticipated sample concentration ranges for the study; but changes to the acceptable spike range should be noted in the study GPO.

8.10 Diluted Sample

Any sample with an integrated analyte peak area greater than that of the ULOQ should be diluted and reanalyzed to attain a result within the limits of quantitation for the batch. It is recommended that sample extracts be diluted at a known ratio with extract from method blanks containing IS at the appropriate level. Alternatively, extraction solvent containing IS at same level as samples may be used to dilute sample extracts.

8.11 Sample Analysis & Analytical Run Format

Samples are typically analyzed in a consistent format, as described below. Other analytical run arrangements such as randomizing calibration standard order in the run are allowed, but should be defined in the study GPO.

8.11.1 System Suitability (optional)

A mid-range calibration standard may be analyzed prior to the calibration curve to verify the system's stability and sensitivity. This standard may be one of the extracted standards or a separate prepared standard. The peak area and retention times should be assessed. It is recommended to shoot one or two solvent blanks before performing system suitability.

System suitability is not required for pass/fail determination of a run, and is simply an evaluation procedure that indicates the instrument's readiness, and can be used to indicate the instrument should be cleaned or maintained before continuing, therefore saving lost time for a potentially bad analytical run. Other quality control aspects of the run following their successful analysis, such as accuracy and precision determined from the results of calibration standards, CCVs and quality control samples in the forms of LCSs and LMSs are the true measure of the performance of an analytical run, not the suitability evaluation.

8.11.2 Instrument Blanks (optional)

Instrument blanks are a zero-volume injection meant to evaluate for interference due specifically to the instrument (solvent lines, solvent, sampler, valves and columns). An empty, cap less vial is usually used as a placeholder on the sample tray for instrument blanks. Instrument blanks are usually injected before or after solvent blanks at the beginning of an analytical run.

8.11.3 Solvent Blanks

Solvent blanks may be extraction solution, Milli-Q™ water or acetonitrile. These injections are evaluated to reduce instrument background before injecting method blanks, especially after an instrument has sat idle for a while.

8.11.4 Method Blanks

Method blanks are injected after injection of solvent blanks or instrument blanks that reduce the instrument background levels. Method blanks are injected just prior to the calibration standards. Typically, three or more method blanks are prepared and injected and their averaged analyte response is used to determine the blank response for LLOQ assignments if calibration blanks are not prepared. When method blanks are prepared with and without IS, the ones without IS should be injected first so that carryover of IS can be evaluated.

Calibration Blanks (optional)

One calibration blank is prepared at the same time, with the same matrix as the calibration standards. Typically, each batch contains six aliquots of the calibration blank, and is analyzed throughout the batch. The average blank response is used to determine the LLOQ.

8.11.5 Calibration Standards

Calibration standards are analyzed from lowest to highest immediately after method blanks and are followed up by analyzing solvent, instrument or method blanks to evaluate for carryover.

8.11.6 Analytical Samples

Up to 10 extracted analytical samples and associated LMSs are injected after the calibration curve and any blanks after the calibration standards, then after 15 analytical samples a set of solvent

blanks and CCVs are analyzed, then up to 10 analytical samples flanked by blanks/CCVs, continuing in that pattern every 10 analytical samples thereafter, as defined below.

8.11.7 Continuing Calibration Verification (CCV)

Continuing calibration verification (CCV) is routinely performed during a run to verify the continued accuracy of the calibration curve over the length of time the analysis is performed on the instrument.

At a minimum, analyze one mid-range calibration standard after every tenth analytical sample, not including solvent blanks, with a minimum of one CCV analyzed at the end of the run. CCVs are typically flanked by solvent blanks or instrument blanks to minimize carry over. Samples must be bracketed by passing CCVs, or by the standard curve and a CCV. Multiple CCV levels may be used if abbreviated curve ranges are anticipated. Different mid-level standards may be rotated during a run to avoid repetitively injecting the same standard too many times and ruining the seal on the cap.

8.12 Percent Moisture Determinations

Soils and sediments require the percent moisture content determined in order to report results on a dry weight (dry wt.) basis, rather than on a native soil (wet wt.) basis. When reporting based on dry weight, percent moisture is determined by drying an accurately weighed soil sample at 105 + 5 °C for 6 to 24 hours. When no difference in mass loss is observed with subsequent weighing and drying cycles then the dry weight is determined, and the loss in mass is attributed to water loss for calculating percent moisture. Percent moisture of soils and sediments can be performed following Attachment-A of this method.

8.13 HPLC Instrument Parameters

8.13.1 Isocratic HPLC

The isocratic high-performance liquid chromatography (HPLC) analysis described herein is useful for the analysis of C4-C12 PFCAs, the PFSAs and FOSA and offers a rapid means with which to perform range finding analyses to aid in LMS preparations and can also serve as a definitive analysis for a more limited analyte set of~5-8 target analytes, including PFBA and PFPeA which do not chromatograph well by the gradient method described below.

Note: The approximately 5-8 target analytes for single injection definitive isocratic analysis does not include their corresponding ISs, hence approximately 16 MRMs for target analytes/ISs may be evaluated with one injection. Because of the short duration of the isocratic HPLC run, evaluating more than 8 analytes with ISs using short dwell times is not practical to get enough scans across a peak, and analyzing more analytes may detract from sensitivity requirements for the analysis. Also, isocratic analysis does not afford separation of linear and branched isomers, should that be desired.

Mobile Phase A (Isocratic HPLC)

Prepare one liter of 1% acetic acid in water using a 10-mL glass volumetric pipette to dispense 10 mL of glacial acetic acid into a one liter volumetric flask and bring to the mark with reagent grade water. Scale the quantity of mobile phase prepared as needed.

Mobile Phase B (Isocratic HPLC)

Prepare one liter of 10 mM ammonium acetate in methanol: acetonitrile (4:1) as mobile phase B by weighing 0.77 grams of ammonium acetate into a one-liter volumetric flask and adding 200 mL of acetonitrile using a 250-mL graduated cylinder. Then bring to the mark with methanol. Scale the quantity of mobile phase prepared as needed.

Table 4. Isocratic HPLC Parameters	
Column Temperature (ºC):	50
Injection Volume (µL):	1 to 100 [a]
Mobile Phase A:	1% Acetic Acid in Water
Mobile Phase B:	10 mM Ammonium Acetate in Methanol
Guard Column (placed after purge valve)	None
Analytical Column (inlet coming from the column switching valve)	Thermo Fischer Scientific Betasil C_8, 4.6 x 150 mm, 5 µm particle size

Table 5. Isocratic HPLC Mobile Phase

Step	Time	A (%)	B (%)	Flow (mL/min)
0	0.00	15	85	1.0
1	4.00	15	85	1.0

8.13.2 Solvent Gradient HPLC Parameters

The gradient HPLC analysis described herein is most useful for the analysis of all analytes in a single injection when the entire analyte list is desired to be measured in one injection, and also is useful for determining linear and branched isomer content for each analyte. The downside of the gradient method is that method performance for PFBA and PFPeA may not be optimal and that the method has a significantly longer cycle time than the isocratic method.

Mobile Phase-A (Gradient HPLC)

Prepare one liter of 2mM ammonium acetate in water using a 10-mL glass volumetric pipette to dispense 10 mL of glacial acetic acid into a 1-L volumetric flask and bring to the mark with reagent grade water. Scale the quantity of mobile phase prepared as needed.

Mobile Phase-B (Gradient HPLC)

Mobile phase-B for gradient HPLC is acetonitrile

Table 6. Gradient HPLC Conditions	
Column Temperature (ºC):	30
Injection Volume (µL):	5 to 25[a]
Mobile Phase A:	1% Acetic Acid in Water
Mobile Phase B:	10 mM Ammonium Acetate in Methanol
Guard Column (placed after purge valve)	Thermo Fischer Scientific Prism™ RP 2x50 mm, 5 µm particle size
Extraction Column (placed prior the analytical column with the outlet directed to the column switching valve)	Waters Corporation, Oasis HLB Online Column, 3 x 20 mm, 25 µm particle size
Analytical Column (inlet coming from the column switching valve)	Thermo Fischer Scientific Betasil C_{18}, 2.1 x 100 mm, 5 µm particle size
[a] If increased sensitivity is desired in order to attain lower LLOQs, injection volumes of up to 50 µL may be used as long as chromatographic peak integrity is maintained (i.e. peak shape, retention time, isomer separation, etc…).	

Table 7. Gradient HPLC Mobile Phase

Step	Time	A (%)	B (%)	Flow (mL/min)
0	0.00	97	3	0.4
1	3.00	97	3	0.4
2	3.50	70	30	0.4
3	17.0	40	60	0.4
5	17.5	10	90	0.4
6	19.5	10	90	0.4
7	20.0	97	3	0.4
8	23.0	97	3	0.4

Scheduled MRMs or period breaks may be used if multiple analytes are being analyzed in one batch.

Note: Other HPLC gradients may be used as long as the method criteria and project data quality objectives are met.

It may be necessary to adjust the HPLC gradient in order to optimize instrument performance. Columns with different dimensions (e.g. 2.1mm x 30mm) and columns from different manufacturers (Keystone Betasil C18 etc.) may be used.

8.13.3 Mass Spectrometer Parameters

Samples are to be analyzed via electrospray ionization in the negative-ion MS/MS mode (MRM mode). The table below provides a list of several PFSAs and PFCAs that may be analyzed using this method and the corresponding MS/MS transitions, and suggested dwell times.

Table 8. MS/MS (MRM) Transitions

Compound	*Analyte Description*	*MRM Transition(s)*	**Dwell Time (ms)*
PFBA (C4 PFCA)	Target	213>169	100
PFPeA (C5 PFCA)	Target	263>219	100
PFHxA (C6 PFCA)	Target	313>269 313>119	100 100
PFHpA (C7 PFCA)	Target	363>319 363>169	50 50
PFOA (C8 PFCA)	Target	413>369 413>219 413>169	50 50 50
PFNA (C9 PFCA)	Target	463>419 463>219 463>169	50 50 50
PFDA (C10 PFCA)	Target	513>469 513>269 513>219	50 50 50
PFUnA (C11 PFCA)	Target	563>519 563>269 563>219	50 50 50
PFDoA (C12 PFCA)	Target	613>569 613>319 613>169	50 50 50
PFBS (C4 PFSA)	Target	299>80 299>99	50 50
PFHS (C6 PFSA)	Target	399>80 399>99	50 50
PFOS (C8 PFSA)	Target	499>80 499>99 499>130	50 50 50
FOSA (C8 PFSA-Sulfonamide)	Target	498>78	50
[1,2,3,4 -$^{13}C_4$]-PFBA	IS for PFBA	217>173	100
[1,2,3,4,5 -$^{13}C_5$]-PFPeA	IS for PFPeA	268>223	100
[1,2 -$^{13}C_2$]-PFHxA	IS for PFHxA	315>270	50
[$^{13}C_4$]-PFHpA	IS for PFHpA	367>322	50
[1,2,3,4,5,6,7,8-$^{13}C_8$]-PFOA	IS for PFOA	421>376	50
[$^{13}C_9$]-PFNA	IS for PFNA	472>427	50
[$^{13}C_6$]-PFDA	IS for PFDA	519>474	50
[$^{13}C_7$]-PFUnA	IS for PFUnA	570>525	50
[1,2 -$^{13}C_2$]-PFDoA	IS for PFDoA	615>570	50
[$^{18}O_2$]-PFBS	IS for PFBS	303>84	50
[$^{13}C_3$]-PFHS	IS for PFHS	402>80	50
[1,2,3,4,5,6,7,8-$^{13}C_8$]-PFOS	IS for PFOS	507>80	50
[$^{13}C_8$]-FOSA	IS for FOSA	506>78	50

*; dwell times listed are suggested and are not optimal. Optimal dwell times depend upon the number of analytes being measured and desired duty cycle time to complete one round of MRM measurement.

Collecting data for multiple mass transitions (MRMs) is a desirable option because summing the signals from multiple MRMs may provide improved sensitivity and improved quantitation of isomers, from which the pseudo-molecular ions of each may fragment with slightly differing ratios the measured fragment masses. Using multiple MS/MS transitions can result in quantitation of isomer (linear and branched) that more closely match to quantitative NMR results for linear and branched isomers. However, the collection of data for a single transition is acceptable if method sensitivity requirements are achieved, and provided that retention time criteria are met to assure adequate specificity.

While not always possible, it is recommended that when looking at a new matrix, that the integrated peak area ratios for the individual MRM transitions for each analyte (for multi-transition analytes only) be analyzed from a matrix-matched standard and that result compared to the result from analysis of an equivalent solvent standard. The results should be reviewed to verify analyte specificity and to rule out matrix interferences which may contribute to or suppress the signal for any of the transitions. A relative percent difference of area count ratios for the MRM transitions between matrix extract and solvent extract of within ±25% indicate that the measured sample results are largely free from significant matrix interferences.

9 Data Analysis and Calculations

For the purposes of simplifying data calculations for concentrations, it will be assumed that the weight of a control standard soil, sediment or sludge, or other matrix, is 1 gram per 1 cc aliquot, despite this may not be the accurate weight of the control matrix.

Calculate the amount of analyte in each soil extract (ng) using the appropriate calibration curve (calculated by plotting a calibration curve as ng of analyte spiked to each 1 cc soil calibration standard versus peak area response),

Calculate the amount of analyte in the 1 cc soil sample aliquot as follows:

$$\text{Soil Sample Analyte Concentration (ng/g)} = \frac{\text{Analytical Result for 1 cc aliquot (ng)}}{\text{Soil Mass of 1 cc aliquot (g)}}$$

Include other dilution factors as appropriate.

Calculate the percent relative standard deviation (%RSD) as follows:

$$\%\text{RSD} = \frac{\text{Standard Deviation}}{\text{Average}} \times 100$$

Where the standard deviation (s) is:

$$s = \sqrt{\frac{n\sum x^2 - \left(\sum x\right)^2}{n(n-1)}}$$

and average is:

$$\text{average} = \frac{1}{n}\sum x$$

The relative percent difference should be calculated as follows:

$$\text{Relative Percent Difference} = \frac{\text{Absolute Value}\left(X_2 - X_1\right)}{\text{Average of } X_2 \text{ and } X_1}$$

Assuming the control matrix is sufficiently devoid of target analytes (i.e. < LLOQ), calculate the percent recovery for the LCS and calibration standards as follows:

$$\text{LCS Percent recovery} = \frac{\text{Amount of analyte measured (ng)}}{\text{Amount of analyte spiked (ng)}} \times 100$$

For LMS and LCS when endogenous analyte levels are measurable above the LLOQ, the percent recovery is calculated as follows:

$$\text{Percent recovery} = \frac{[\text{measured conc. in spiked sample (ng/g)}] - [\text{measures conc. in non - spiked sample (ng/g)}]}{\text{Amount of analyte spiked (ng/g)}} \times 100\%$$

10 Method Performance Criteria

10.1 System Suitability Criteria

This method does not require the evaluation of system suitability prior to analysis. However, in the event the analyst wishes to perform suitability evaluation by replicate injections of a calibration standard, the following recommended criteria are offered as guidance to evaluate suitability injections should it be determined applicable to evaluate them. Triplicate, or more, injections of a suitability standard should have peak area count ratios (analyte area counts/IS area counts) with an RSD ≤20% between injections and a retention time analyte peak drift with RSD ≤5%.

10.2 Calibration Criteria

The coefficient of determination (R^2) value for the fitted calibration curve must be greater than or equal to 0.990 [or a correlation coefficient (R) of > 0.995]. If the calibration curve does not contain at least a minimum of six passing standards, the batch should be reanalyzed or re-prepared. Passing standards, when back-calculated from the curve, shall fall within 100% ± 30% (± 35% at LLOQ) for extracted curves and 100% ± 25% (± 30% at LLOQ) for solvent curves. Calibration standards falling outside these limits should be excluded from the calibration.

10.3 Continuing Calibration Verification (CCV) Criteria

CCVs should be within 100% ± 30% (± 35% at LLOQ) for extracted CCVs and ± 25% (± 30% at LLOQ) for solvent curves. Samples not bracketed by passing CCVs or the standard curve and a CCV should be reanalyzed.

10.4 Sensitivity Criteria

If extracted matrix-matched matched calibration is used, the analyte response (peak area counts) for the standard defining the low limit of quantitation (LLOQ) for each analyte shall be at least two times the analyte response of the control matrix blanks (procedural blanks) or calibration blanks (if prepared). If triplicate results for procedural blank analytical responses produce a RSD ≤ 50%, then the average matrix blank response may be used to evaluate the LLOQ. However, if the RSD is greater than 50%, the largest matrix blank response will be used for the comparison (i.e., the response of the LLOQ must be greater than two times the highest matrix blank response).

If solvent calibration is used, the same criteria described above shall be used except that extract solution blanks will be used for the evaluation instead of procedural blanks. Endogenous levels in the control matrix (matrix blanks spiked with IS) may be quantitated using the solvent calibration if method precision and accuracy criteria are met.

10.5 LCS Accuracy Criteria

LCS samples shall be within ± 30% of their respective nominal value. If the average recovery of a LCS falls outside method acceptance, but at least 50% (1/2) of LCSs at the same level and at least 67% (2/3) of LCS samples in the batch are within 100 ± 30% of their respective nominal value the results of the batch may be reported.

All LCS samples will be control charted as per ETS-4-026 for determination of analytical method uncertainty.

If more than 50% of LCSs at one level or more than 33% of the LCS samples in the batch fail to meet method acceptance criteria, the affected data should not be reported.

Three levels of LCS per batch are recommended, and each level in triplicate. However, it is likely that one level may need to be disregarded because that spike level could fall below an adjusted LLOQ or above an adjusted ULOQ. Ideally, each preparation batch should have three usable levels of LCSs. In such instances, the acceptance of the data will be determined on a case-by-case basis.

If the control matrix has measurable levels of target analytes, the LCS concentrations should be adjusted to account for the endogenous levels present. Ideally, the matrix used for LCS preparations will be the calibration matrix, or other matrix sufficiently devoid of target analytes. Endogenous concentrations may be determined by method of standard addition (extracted calibration) or by quantitation of the matrix blanks spiked with ISs (solvent calibration).

10.6 LMS Accuracy Criteria

This is a performance based method which utilizes LMSs for determining sample specific measurement accuracy. Target analyte recoveries should be within 100 ± 30% of their respective spiked value. However, samples producing matrix spike recoveries outside of 100 ± 30% will be considered on an individual basis or may be defined with broader acceptance for the study in the GPO or Protocol. However, the following approaches are offered as a guide to handle such cases:

1) Results can be reported if recovery is within 100 ± 50%, however, the affected sample results with LMS outside of 100 ± 50% will be flagged and footnoted appropriately in the final report and assigned a sample-specific analytical uncertainty adjusted to reflect the LMS recovery.

2) If LMS recovery is outside of 100 ± 50%, the sample results will not be reported. A footnote in the data table in the final report will indicate the results are not reported (NR) due to QC failure.

3) If LMS failure is observed to be due to insufficient or inappropriate spiking levels, the samples and associated LMSs may be re-prepared at an appropriate spike level and reanalyzed (reassayed). This approach should be considered if the original LMSs were prepared at levels inappropriate relative to the samples endogenous concentrations (i.e. spike level was less than one-half the endogenous level or more than 20-times the endogenous level). Depending on the results of the reanalysis, sample results may or may not be reported as per reasons (1) or (2) above.

10.7 Precision Criteria

Method precision triplicate sample results will be evaluated by calculating the relative standard deviation (%RSD). The percent RSD for each analyte shall be within ± 20% for all LCSs (collectively). Precision data outside ± 20% may be flagged and reported as outside method acceptance criteria. The report will address this departure from method criteria.

10.8 Sample Duplicate Precision Criteria

The sample and sample duplicate precision should have a relative percent difference within 20%. If the relative percent difference is not within 20% for these two samples, the results will be reported and footnoted as having a RPD of greater than 20%.

10.9 Analytical Method Uncertainty Calculation

As part of the 3M EHS Laboratory ISO17025 (A2LA) accreditation, control charting of the LCS results from analytical runs employing this method will be required once added to the scope of accreditation. The analytical method uncertainty should be determined based on the accumulated historical LCS data as per ETS-12-012.

In some instances, it may be desirable to report a study specific method uncertainty using only the LCSs analyzed as part of a study; this is acceptable and should be defined in the GPO or study protocol prior to reporting the uncertainly in this fashion.

A sample-specific expanded uncertainty may be assigned to individual sample results based on an associated LMS recovery result, when warranted. For example, a sample with LMS recovery of 38% may be reported with expanded uncertainty of ± 38%, when LCS uncertainty may indicate a smaller uncertainty range.

11 Pollution Prevention and Waste Management

The laboratory procedures for disposal of regulated and non-regulated soils should be followed

Flammable solvent waste is disposed of in high BTU containers.

Glass pipette waste is disposed of in “broken glass” containers located in the laboratory.

Regulated soils are shipped, handled & discarded according to laboratory SOP ETS-4-033

12 Records

Use the appropriate prep sheet or equivalent to record the pertinent data. Other information should be documented as appropriate.

13 References

ETS-4-026 Control Charts for Laboratory Analyses

ETS-4-033 Regulated Soils Sample Shipping, Receipt, and Handling

ETS-12-012 Estimation of Uncertainty of Measurements

14 Revisions

Revision Number	Summary of Changes
1	The entire method was updated, including the title and major changes to accommodate isocratic analysis and to include validation information. Updated the title to reflect C4 and C5 carboxylic acids can also be analyzed by this method. Updated the scope/application Section 1 with some minor rewording. Updated the abbreviation PFASs to be more accurately and correctly reflected as “PFSAs” for perfluorinated sulfonates, since the abbreviation “PFAS” is more commonly used in literature to stand for the broader class known as perfluoroalkyl substances. Updated text and appropriate sections by adding isocratic settings for range-finding analyses and for use in definitive analyses of limited analyte sets; including PFBA and PFPeA in those analyte sets. Added Sample and Extract Storage and Stability section. Updated definitions and analytical procedures sections.