

## Perfluorinated Alkyl Acids (PFAA) in Soils by LC/MS/MS - PBM

**Parameter** Perfluorinated Alkyl Acids (Perfluorobutane Sulphonate (PFBS), Perfluorooctane Sulphonate (PFOS), Perfluorooctanoic Acid (PFOA)) in Soils

**Analytical Method** Methanol Extraction, Solid Phase Extraction (SPE) Clean-up, LC//MS/MS

**Introduction** This method is applicable to the quantitative determination of perfluorinated alkyl substances in soils and solids.

**Method Summary** Soil samples are spiked with surrogates, extracted with a methanol solution, cleaned up and concentrated by SPE. Analysis for PFBS, PFOS and PFOA is by reversed phase liquid chromatography, isotope dilution tandem mass spectrometry (LC/MS/MS).

This method may be applied to other perfluorinated alkyl acids in soils provided the performance requirements and data quality objectives are met.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided all stated performance requirements and prescribed (mandatory) elements are met.

<b>MDL(s) and EMS Analyte Codes</b>	<b><u>Analyte</u></b>	<b><u>CAS No.</u></b>	<b><u>Approx. MDL (µg/g)</u></b>	<b><u>EMS Analyte Code</u></b>
	Perfluorobutane Sulphonate (PFBS)	375-73-5		
	Perfluorooctane Sulphonate (PFOS)	1763-23-1		
	Perfluorooctanoic Acid (PFOA)	335-67-1		

**EMS Method Code(s)** Refer to [EMS Parameter Dictionary](#) on the ministry website for all current EMS codes.

**Matrix** This method is applicable to the determination of perfluorinated alkyl acids in extracts prepared from all types of solid waste matrices and soil samples.

## Interferences and Precautions

- a) All reagents and solvents should be pesticide residue purity or higher to minimize interference problems. Avoid the use of PFC-containing caps.
- b) Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably depending on variations in the sample matrices. Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.
- c) Contaminants have been found in reagents, glassware, tubing, glass disposable pipettes, filters, degassers, and other apparatus that release perfluorinated compounds. These materials and supplies must be demonstrated to be free from interferences by analysis of laboratory reagent blanks under the same conditions as the samples. If found, take measures to remove the contamination or qualify the data; background subtraction of blank contamination is not allowed.
- d) Use polyethylene LC vial caps, polyethylene disposable pipettes or any other target-analyte-free materials. Check disposable pipettes for release of target analytes of interest.
- e) The Liquid Chromatography system used should consist, as much as practical, of sample solution or eluent-contacting components free of PFC target analytes of interest.
- f) Degassers are important to continuous LC operation and most commonly are made of fluorinated polymers. To enable use, an isolator column should be placed after the degasser and prior to the sample injection valve to separate the PFCs in the sample from the PFCs in the LC system.

## Sample Handling and Preservation

**Container:** Glass or polypropylene. Avoid PTFE.

**Preservation:** None. Maintain samples at  $\leq 10^{\circ}\text{C}$  during transport.

## Stability

**Holding Time:** Analyse within 28 days of collection.

**Storage:** Refrigerate samples at  $\leq 6^{\circ}\text{C}$ .

## Procedure

### Calibration Standard Stock:

If possible, purchase the method analytes as technical grade standards or neat materials. Standards or neat materials that contain only the linear isomer can be substituted only if technical grade (linear and branched isomers) standards or neat material cannot be purchased. PFOS must be purchased as technical grade (containing branched and linear isomers).

### Extraction:

A summary of the extraction method is as follows:

- a) Weigh and transfer a representative aliquot of the sample to a polypropylene tube.
- b) Add isotopically-labelled surrogates and isotope dilution standards to samples and quality control samples.
- c) Extract samples with a methanol:water extraction solution.
- d) Following extraction, centrifuge the tubes.
- e) Filter or decant the supernatant.
- f) Adjust the extract to pH 4-5.
- g) Process the extract through a conditioned SPE column.
- h) Transfer an aliquot to an autosampler vial, add isotopically-labelled internal standard and analyse the extract by LC/MS/MS.

Detailed extraction procedures are available in the following reference.

- ASTM D7968-14, Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry

(LC/MS/MS), ASTM International, West Conshohocken, PA, 2014

**Instrumental Analysis:**

Detailed instrumental procedures are not provided in this method. The procedures described in the above reference are suitable for general guidance.

Extracts must be analysed by LC/MS/MS. A C<sub>18</sub> column or any column that provides adequate resolution, peak shape, capacity, accuracy and precision is used.

Use a five-point initial calibration (four point minimum) over the desired working range to meet the performance requirements outlined in ASTM D7968-14.

Most PFAAs are produced by two different processes. One process gives rise to linear PFAAs only while the other process produces both linear and branched isomers. Thus, both branched and linear PFAAs can potentially be found in the environment. For the compounds that give rise to more than one peak, all the chromatographic peaks observed in the standard must be integrated and the areas totaled. Chromatographic peaks in a sample must be integrated in the same way as the calibration standard.

**Performance Requirements**

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements and apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method revalidation studies. For Initial Validations, averages of at least 8 Laboratory Control Samples or Reference Materials must be assessed. Ongoing Revalidations (performance reviews) should assess QC data encompassing longer periods (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Revalidations.

**Accuracy Requirement:** Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Recovery must be between 70-130% of true value.

**Precision Requirement:** Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples at concentrations above ten times the MDL. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

**Sensitivity Requirement:** Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

**Quality Control**

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	50-140%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	≤50% RPD [or absolute difference < 2x DL for low level results]
Matrix Spike (MS) or Reference Material	One per batch (max 20 samples)	50-140%
Isotope Dilution Standards	All samples	Absolute recovery of all isotope dilution standards used for recovery correction must be 10% - 130%.
Surrogate Compounds	All samples	50-140%

Internal Standards (not used in isotope dilution calculations)	All samples	50-200% Retention times of internal standards should be within $\pm 6$ seconds of retention times in the associated CCV.
Isotope Dilution Compounds	For each analyte	10-130%
Calibration Verification Standard (CVS)	minimum 1 per initial calibration	70-130%
Continuing Calibration Verification (CCV)	Every 12 hours within an instrument run and at the end of each run	70-130%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

**Method Blank:** Required. Prepare a Method Blank using clean oven-baked sand.

**Laboratory Duplicates:** Required. Data quality objectives are listed above.

**Laboratory Control Sample (Method Spike):** Required. Prepare a Laboratory Control Sample by fortifying clean sand with known concentrations of the analytes.

**Matrix Spike:** Required. Spike a duplicate sample with known concentrations of the analytes.

**Surrogate Compounds:** Required. Surrogates must be stable isotopically-labelled analogues of the compounds of interest. Surrogates are added to the sample prior to extraction.

Isotope Dilution Standards: Isotope dilution standards must be stable isotopically-labelled analogues of the compounds of interest

**Calibration Verification Standard (CVS):** Required. A CVS from a source separate from the calibration standard must be analyzed with each initial calibration to monitor calibration accuracy.

**Continuing Calibration Verification (CCV):** Required. A mid-point calibration standard must be analyzed throughout the instrument run at least every 12 hours and at the end of the run to monitor calibration drift. A CVS may serve the same purpose.

**Prescribed Elements** The following components of this method are mandatory:

1. Analysis must be by LC/MS/MS. Initial calibrations must include at least 4 points.
2. All Performance Requirements and Quality Control requirements must be met.
3. Isotope dilution recovery correction must be used. Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are used.

- References**
1. ASTM D7968-14, Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), ASTM International, West Conshohocken, PA, 2014
  2. US EPA Method 537, Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), version 1.1, Sept/2009
  3. US EPA Chapter 4, "Organic Analytes", SW-846 Update V Revision 5, July 2014

**Revision History** July 10, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.