# Perfluoroalkyl Substances (PFAS) in Soils by LC/MS/MS - PBM

**Parameter**

Perfluoroalkyl Substances (Perfluorobutane Sulfonate (PFBS), Perflourooctane Sulfonate (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 isotope dilution standards, extracted with a methanol solution, and cleaned up and concentrated by SPE. Analysis for PFBS, PFOS and PFOA is by reversed phase liquid chromatography with 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.

**MDL(s) and EMS Analyte Codes**

| Analyte | CAS No. | Approx. MDL (µg/g) | EMS Analyte Code |
|---|---|---|---|
| Perfluorobutane Sulfonate (PFBS) | 375-73-5 | 0.001 – 0.01 | Defined on request |
| Perflourooctane Sulfonate (PFOS) | 1763-23-1 | 0.001 – 0.01 | Defined on request |
| Perfluorooctanoic Acid (PFOA) | 335-67-1 | 0.001 – 0.01 | Defined on request |

**EMS Method Code(s)**

***Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.

**Matrix**

Soil, Sediment, Sludge, Solid Waste.

**Interferences and Precautions**

a) All reagents and solvents should be pesticide residue purity or higher to minimize interference problems. Avoid the use of all sources of Teflon®/PTFE including 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 for tested samples. If found, take measures to remove the contamination or qualify the test results; 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 PTFE and PFC target analytes.

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 plastic (HDPE or Polypropylene recommended). Avoid PTFE.

**Preservation**: None. Cool samples immediately after sample collection.

**Stability**

**Holding Time:** Extract samples within 28 days of collection (Ref: ASTM D7968-14). Sample extracts may be held for up to 40 days before instrumental analysis.

**Storage**: Store samples at ≤ 10°C during shipment to the laboratory and at ≤ 6°C at the laboratory. Avoid freezing to prevent sample breakage. Storage of extracts and standards at room temperature is preferred to prevent sorption onto container surfaces when refrigerated. However, standards and extracts may be stored refrigerated if stabilized at room temperature prior to use (Ref: EPA 537).

**Procedure**

**Calibration Standard Stock**:

If possible, purchase all calibration standards 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 suitable neat technical materials cannot be purchased. PFOS calibration standards must be purchased as technical grade (containing branched and linear isomers).

**Extraction**:

Detailed sample extraction procedures are not provided in this method. Consult ASTM Method D7968-14 for more detailed guidance (see references). 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 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 injection internal standard and analyze the extract by LC/MS/MS.

**Instrumental Analysis**:

Detailed instrumental procedures are not provided in this method. Consult EPA Method 537 or ASTM Method D7968-14 for more detailed guidance (see references).

Extracts must be analyzed by LC/MS/MS. A $C_{18}$ column or any column that provides adequate resolution, peak shape, capacity, accuracy and precision is used.

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

If required, dilutions may be conducted on high level samples using the standard isotope dilution corrections if the diluted ID standards can still be accurately measured. Alternatively, a smaller (but representative) portion of sample may be extracted and analyzed, or higher amounts of the ID standards may be added prior to extraction. For highly contaminated soils, ID standards may be added to a quantitative fraction of the soil extract, rather than being added to the soil prior to extraction (e.g. add the normal amount of ID standards to $1/100^{th}$ of the soil extract to accomplish a 100-fold dilution).

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 (particularly PFOS), 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 within 2x reported DL for low level results] |
| Matrix Spike (MS) | One per batch (max 20 samples) | 50-140% |
| Peak Asymmetry Factor | Calculate the peak asymmetry factor for the first two eluting chromatographic peaks in a mid-level calibration standard every time a calibration curve is generated. | 0.8–1.5 (Ref: EPA 537) |
| Injection Internal Standard (IIS) (not used in isotope dilution calculations) | All samples | Peak area counts for all internal standards in all injections must be within ± 50% of the average peak area calculated during the initial calibration and 70-140% from the most recent CCV (Ref: EPA 537). |
| Isotope Dilution Standards (IDS) | All samples, all regulated PFAS analytes | Absolute recovery of all isotope dilution standards used for recovery correction must be 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 (MB):** Required. Prepare a Method Blank using clean oven-baked sand, treated exactly like a sample including exposure to equipment, solvents and reagents, and the internal standards (IDS and IIS) that are used in the analysis batch.

**Laboratory Duplicate (DUP):** Required. Data quality objectives are listed above.

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

**Matrix Spike (MS):** Required. Spike a duplicate field sample with known concentrations of the target analytes.

**Injection Internal Standard (IIS):** One or more injection internal standards are added to extracts at the end of the extraction process. IIS's should be stable isotopically-labelled PFAA substances representative of method analytes. They are used to monitor the integrity of each injection, and to calculate absolute recoveries of isotope dilution standards in samples and QC.

**Isotope Dilution Standards (IDS)**: Isotope dilution standards must be stable isotopically-labelled analogues of the parameters of interest. Isotope Dilution Standards are added to the sample prior to extraction and are used for correction of extraction recoveries and matrix effects. Isotope Dilution is required for all regulated PFAS analytes (PFOS, PFOA, PFBS), and is recommended for other PFAS analytes. If suitable labelled isotopes are unavailable for non-regulated PFAS analytes, then the use of the most chemically similar available IDS is recommended.

**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. At least two MRM transitions are required to be monitored for PFOS and PFOA (only one suitable transition exists for PFBS). Labs must define appropriate criteria for confirmation of analyte identity by secondary transitions.
2. Initial calibrations must include at least 5 points.
3. PFOS test results must represent and include the sum of all branched and linear isomers that are identifiable from technical grade PFOS standards or material.
4. The 499 to 80 m/z MRM transition must be used for the quantitation of PFOS, unless subject to sample specific interferences.
5. Isotope dilution calibration and recovery correction must be used for all regulated PFAS analytes.
6. Blank correction is not permitted for this method.
7. All Performance Requirements and Quality Control requirements must be met.
8. Sample container materials, preservation, storage, and hold time guidance may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

**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, 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


**Revision History**

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.