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

Parameter

Perfluorinated Alkyl Acids (Perfluorobutane Sulphonate (PFBS), Perflourooctane Sulphonate (PFOS), Perfluorooctanoic Acid (PFOA)) in Waters

Analytical Method

Solid Phase Extraction (SPE), LC/MS/MS

Introduction

This method is applicable to the quantitative determination of perfluorinated alkyl substances in waters.

Method Summary

Water samples are fortified with surrogates and passed through an SPE cartridge to extract the method analytes and surrogates. The compounds are eluted from the solid phase with methanol and the extract is evaporated to dryness. Internal standard is added and the volume adjusted with to 1 mL with methanol:water. Analysis for PFBS, PFOS and PFOA is by isotope dilution liquid chromatography tandem mass spectrometry (LC/MS/MS).

This method may be applied to other perfluorinated alkyl acids in waters 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 Sulphonate (PFBS)	375-73-5		
Perflourooctane 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 water 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 the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent. Total organic carbon (TOC) is a good indicator of humic content of the sample.

c) Contaminants have been found in reagents, glassware, tubing, glass disposable pipettes, filters, degassers, aluminum foil, PTFE products 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) Relatively large quantities of the preservative may be added to sample bottles. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks particularly when new lots of reagents are acquired.

e) SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

f) 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.

g) 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.

h)

Sample Handling and Preservation

Container: Polypropylene. Other plastic materials that meet QC requirements may be used. Avoid PTFE.

Preservation: Preservation is not required. Samples may be preserved with sodium bisulphate to pH <2. If chlorine is present or suspected in the samples, they may be preserved with sodium thiosulphate or Tris base (Trizma®) at 5 g/L.

Maintain samples at ≤10°C during transport.

Stability

Holding Time:

Samples: Extract preserved samples within 14 days of collection. Extract unpreserved samples within 7 days of collection.

Extracts: May be held for up to 28 days before instrumental analysis.

Storage: Refrigerate samples at ≤6°C; do not freeze. Store extracts at room temperature.

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) Transfer a representative aliquot of sample to a suitable pre-calibrated container. (An

indirect measurement may be made by marking the level of the sample on the bottle or by weighing the sample and bottle.) Because some PFAAs adsorb to surfaces, do not transfer the sample to a graduated cylinder for volume measurement.

b) Add isotopically-labelled surrogates to samples and quality control samples.

c) Pass the samples through a conditioned SPE column and extract with a methanol solution.

d) Concentrate the extract to dryness under a gentle steam of nitrogen in a water bath to remove all the water/methanol mix.

e) Add isotopically-labelled internal standard and reconstitute to 1 mL with methanol:water solution.

f) Transfer an aliquot to a polypropylene autosampler vial and analyse by LC/MS/MS.

Detailed extraction and instrumentation procedures are available in the following reference:

- 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

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_{18} column or any column that provides adequate resolution, peak shape, capacity, accuracy and precision is used.

Use a five-point initial calibration over the desired working range to meet the performance requirements outlined in US EPA Method 537.

Adjust the final analyte concentration to reflect the actual sample volume used for extraction.

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.

As noted above, PFOS (and most likely PFBS) has linear and branched isomers. In an attempt to reduce PFOS bias, it is required that the transition m/z 499 → m/z 80 be used as the quantitation transition. Some MS/MS instruments, such as conventional ion traps, may not be able to scan a product ion with such a wide mass difference from the precursor ion; therefore, they may not be used for this method if PFOS, PFBS, or PFHxS analysis is to be conducted.

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 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 the 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)	70-130%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	≤30% RPD [or absolute difference < 2x DL for low level results]
Matrix Spike (MS)	One per batch (max 20 samples)	70-130%
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
Surrogate Compounds	All samples	70-130%
Internal Standards (not used in isotope dilution calculations)	All samples	Peak area counts for all internal standards in all injections must be within 50-200% of the average peak area calculated during the initial calibration and 70-140% from the most recent CCV
Isotope Dilution Compounds	For each analyte	10-130%
Calibration Verification Standard (CVS)	Minimum 1 per initial calibration	70-130%
Continuing Calibration Verification (CCV)	One per batch (max 20 samples)	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. An aliquot of reagent water that is treated exactly like a sample including exposure to equipment, solvents and reagents, sample preservatives, internal standard and surrogates that are used in the analysis batch .

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

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

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

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

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

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 20 samples and at the end of the run to monitor calibration drift.

Prescribed Elements

The following components of this method are mandatory:

1. Analysis must be by LC/MS/MS. Initial calibrations must include at least 5 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. 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
2. 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.