



Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

UCT Product:

ECDVB156P- Enviro-Clean[®] DVB 500 mg, 6 mL cartridge, PE Frit

or

ECHLD156-P - Enviro-Clean[®] HL DVB 500 mg, 6 mL cartridge, PE Frit

EPA Method 537 Version 1.1

Method 537 Analytes

Analyte	Acronym	CASRN
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	--
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	--
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8

Interferences

- Do not cover glassware with aluminum foil because PFAAs can be potentially transferred from the aluminum foil
- PFAA standards, extracts and samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass
- PFAA analyte, IS and SUR standards commercially purchased in glass ampoules are acceptable however all subsequent dilutions must be prepared and stored in polypropylene containers

- The method analytes in this method can also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil and SPE sample transfer lines. These items must be routinely demonstrated to be free from interferences (less than 1/3 the MRL for each method analyte) under the conditions of the analysis by analyzing laboratory reagent blanks
- 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. Total organic carbon (TOC) is a good indicator of humic content of the sample

Preservation Reagent

Compound	Amount	Purpose
Trizma®*	5.0 g/L	Buffer & free Cl removal

* Synonym: TRIS HCl (Tris(hydroxymethyl)aminomethane hydrochloride) CASRN 1185-53-1

Internal Standards and Surrogates

Internal Standards	Acronym
Perfluoro-[1,2- ¹³ C ₂]octanoic acid	¹³ C-PFOA
Sodium perfluoro-1-[1,2,3,4- ¹³ C ₄]octanesulfonate	¹³ C-PFOS
N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid	d ₃ -NMeFOSAA

Internal Standard (IS) Primary Dilution Table

IS	Conc. of IS Stock (µg/mL)	Vol. Of IS Stock (µL)	Final Vol. of IS PDS (µL)	Final Conc. of IS PDS (ng/µL)
¹³ C-PFOA	1000	5.0	5000	1.0
¹³ C-PFOS	50	300.0	5000	3.0
d ₃ -NMeFOSAA	50	400.0	5000	4.0

Surrogates	Acronym
Perfluoro-n-[1,2- ¹³ C ₂]hexanoic acid	¹³ C-PFHxA
Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid	¹³ C-PFDA
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid	d ₅ -NEtFOSAA

Surrogate Primary Dilution Table

SUR	Conc. Of SUR Stock (µg/mL)	Vol. of SUR Stock (µL)	Final Vol. of SUR PDS (µL)	Final Conc. Of SUR PDS (ng/µL)
¹³ C-PFHxA	50	100.0	5000	1.0
¹³ C-PFDA	50	100.0	5000	1.0
d ₅ -NEtFOSAA	50	400.0	5000	4.0

Analyte Solvent Dilution Table

Analyte	Analyte Stock Solvent
PFHxA	96:4% (vol/vol) methanol:water
PFHpA	96:4% (vol/vol) methanol:water
PFOA	96:4% (vol/vol) methanol:water
PFNA	96:4% (vol/vol) methanol:water
PFDA	96:4% (vol/vol) methanol:water
PFUnA	96:4% (vol/vol) methanol:water
PFDoA	96:4% (vol/vol) methanol:water
PFTTrDA	100% ethyl acetate
PFTA	100% ethyl acetate
PFBS	100% methanol
PFHxS	100% methanol
PFOS	100% methanol
NEtFOSAA	100% methanol
NMeFOSAA	100% methanol

Internal Standard Primary Dilution (IS PDS) Standard

Prepare (or purchase) IS PDS at a suggested concentration of 1-4 ng/ μ L in 96:4% (vol/vol) methanol:water. Use 10 μ L of this 1-4 ng/ μ L solution to fortify the final 1-mL extracts. This will yield a concentration of 10-40 pg/ μ L of each IS in the 1-mL extracts.

Procedure

1) Cartridge Preparation

- Insert a **ECDVB156P/ ECHLD156-P** cartridge in a vacuum manifold or automated extraction system
- Add 15 mL of methanol to the cartridge and slowly draw through under vacuum

Note: Do not let the cartridge dry out after addition of methanol otherwise start over

- Add 18 mL of reagent water
- Draw through under vacuum but do not let water level drop below cartridge frit

2) Sample Extraction

- Adjust vacuum setting to achieve a flow rate of about 10-15 mL/min
- Draw water through sample cartridge
- After sample extraction, rinse sample bottles and reservoir with 2 x 7.5 mL aliquots of reagent water and add to cartridge
- Dry cartridge by drawing air through it for 5 minutes at high vacuum

3) Sample Elution

- Insert a polypropylene (PP) collection tube in the vacuum manifold
- Rinse sample bottle and reservoir with 4 mL of methanol and add to cartridge
- Draw through cartridge in dropwise manner

- d. Rinse sample bottle and reservoir with another 4 mL of methanol and add to the cartridge
- e. Draw through cartridge in dropwise manner

4) Extract Concentration

- a. Concentrate the extract to dryness using a gentle stream of N₂ in a heated water bath 60-65° C
- b. Add the appropriate amount of 96:4% (vol/vol) methanol:water solution and the IS PDS to the collection vial
- c. Bring the volume to 1 mL and vortex
- d. Transfer a small aliquot with a plastic pipette to a polypropylene autosampler vial

NOTE: Do not transfer the entire 1-mL aliquot to the autosampler vial because the polypropylene autosampler caps do not reseal after injection. Do not store the extracts in the autosampler vials as evaporation losses can occur. Extracts can be stored in 15-mL centrifuge tubes

5) HPLC Analysis Conditions

LC Method Conditions

Time (min)	% 20 mM	% Methanol
Initial	60.0	40.0
1.0	60.0	40.0
25.0	10.0	90.0
32.0	10.0	90.0
32.1	60.0	40.0
37.0	60.0	40.0
Flow rate of 0.3 mL/min		10 µL injection
Waters Atlantis® dC ₁₈ 2.1 x 150 mm packed with 5.0 µm C ₁₈ stationary phase or equivalent		

ESI-MS Conditions

Polarity	Negative Ions
Capillary Needle Voltage	-3 kV
Cone Gas Flow	98 L/hr
Nitrogen Desolvation Gas	1100 L/hr
Desolvation Gas Temperature	350° C

MS/MS Method Conditions					
Segment	Analyte	Precursor Ion (m/z)	Product Ion (m/z)	Cone Voltage	Collision Energy (v)
1	PFBS	299	80	40	25
2	PFHxA	313	269	15	10
3	PFHpA	363	319	12	10
3	PFHxS	399	80	40	40
4	PFOA	413	369	15	10
4	PFNA	463	419	12	10
4	PFOS	499	80	40	40
5	PFDA	513	469	15	10
5	NMeFOSAA	570	419	25	20
5	NEtFOSAA	584	419	25	20
5	PFUnA	563	519	15	10
5	PFDoA	613	569	15	10
6	PFTA	663	619	15	10
6	PFTA	713	669	15	10
2	¹³ C-PFHxA	315	270	15	10
5	¹³ C-PFDA	515	470	12	12
5	d ₅ -NEtFOSAA	589	419	25	20
4	¹³ C-PFOA	415	370	15	10
4	¹³ C-PFOS	503	80	40	40
5	d ₃ -NMeFOSAA	573	419	25	20

Summarized 15 from: Shoemaker, J.A., Grimmert P.E., Boutin, B.K., 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, September 2009, National Exposure Research Laboratory, Office Of Research And Development, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268

Listing of instrument manufacturers does not constitute endorsement by UCT

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