

Analysis of Per- and Polyfluoroalkyl Substances in Wastewater Using Draft EPA Method 1633 with Semi-Automated Solid Phase Extraction

Introduction

Per- and polyfluoroalkyl substances (PFAS) is a general term used to describe compounds that are largely comprised of or contain a perfluorinated or polyfluorinated carbon chain moiety such as $F(CF_2)_n-$ or $F(CF_2)_n-(C_2H_4)_n$.

Perfluorooctane sulfonate (PFOS) and other PFAS are widely used in industrial and consumer applications, including stain-resistant coatings for textiles, leather, and carpets; grease-proof coatings for paper products approved for food contact; firefighting foams; mining and oil-well surfactants; floor polishes; and insecticide formulations.

In recent years, there has been increasing concern over the levels of PFAS such as PFOS and PFOA (perfluorooctanoic acid) in the global environment and their fate and possible adverse effects.

Recent developments in the US regarding PFAS methods include EPA method 1633 which is currently in a draft stage and will allow for analysis of wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue as matrices.

To meet demands for a low-cost method that requires less financial investment than fully automated systems, FMS developed a simple semi-automated system which is fast, inexpensive and yields high quality data.

Instrumentation

- FMS EZPFC® System
- Vacuum pump
- Agilent 6475 TripleQuad LC/MS

Consumables

- Agilent Bond Elut PFAS WAX 250 mg cartridges
- Ultrapure DI water
- Methanol pesticide grade
- Ammonium hydroxide
- Formic acid
- Relevant PFAS spiking standards

Method

- Twelve synthetic wastewater samples (500 mL) spiked with 50 ppt native PFAS standards and relevant internals
- Load sample bottles onto system and install cartridges
- Fill rinse bottles with 5 mL reagent water
- Turn on vacuum (stays on rest of procedure)

Stage 1

- Condition cartridges with 15 mL 1% methanolic ammonium hydroxide, followed by 5 mL of 0.3M formic acid.
- Load samples across the cartridges at 5-10 mL/min (~ 8-inch Hg)
- Sample bottles rinsed with 5 mL reagent water (twice), followed by 5 mL of 1:1 0.1M formic acid/methanol (using nitrogen)
- Rinses loaded across cartridges
- Dry 15 sec under vacuum

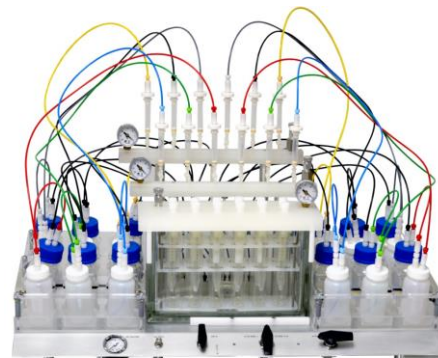
Stage 2

- Rinse sample bottles with 5 mL 1% methanolic ammonium hydroxide
- Load rinses across cartridges and collect in polypropylene tubes
- As per the method no further concentration is carried out.

Further relevant standards were added prior to LC/MS analysis.

Analysis

- Take aliquot from final 5 mL extract
- Analyze with LC/MS



FMS EZPFC system



Compound	Average (%)	RSD (%)
PFBA	96	1%
PFPeA	95	2%
PFHxA	96	3%
PFHpA	95	1%
PFOA	96	3%
PFNA	98	2%
PFDA	98	2%
PFUnA	96	1%
PFDoA	97	3%
PFTrDA	89	4%
PFTeDA	99	2%
PFBS	98	3%
PFPeS	99	1%
PFHxS	103	2%
PFHpS	100	6%
PFOS	101	4%
PFNS	97	3%
PFDS	89	4%
PFDoS	74	8%
4:2FTS	95	1%
6:2FTS	98	4%
8:2FTS	92	4%
PFOSA	99	2%
NMeFOSA	90	9%
NEtFOSA	92	2%
NMeFOSAA	98	4%
NEtFOSAA	97	5%
NMeFOSE	93	6%
NEtFOSE	92	6%
HFPO-DA	99	5%
ADONA	97	5%
PFMPA	96	1%
PFMBA	95	2%
NFDHA	94	6%
9Cl-PF3ONS	96	4%
11Cl-PF3OUdS	82	5%
PFEESA	95	3%
3:3 FTCA	101	3%
5:3 FTCA	97	2%
7:3 FTCA	95	3%

Table 1. Average recoveries (%) and RSDs (%) for 40 native PFAS in synthetic wastewater (1633).



Compound	Average	RSD (%)
13C4-PFBA	111	6%
13C5-PFPeA	116	6%
13C5-PFHxA	110	6%
13C4-PFHpA	110	7%
13C8-PFOA	107	6%
13C9-PFNA	109	8%
13C6-PFDA	106	9%
13C7-PFUnA	104	10%
13C2-PFDoA	93	10%
13C2-PFTeDA	83	12%
13C3-PFBS	106	6%
13C3-PFHxS	105	11%
13C8-PFOS	110	8%
13C2-4:2FTS	99	15%
13C2-6:2FTS	97	16%
13C2-8:2FTS	105	19%
13C8-PFOSA	142	15%
D3-NMeFOSA	114	12%
D5-NEtFOSA	70	16%
D3-NMeFOSAA	103	9%
D5-NEtFOSAA	111	14%
D7-NMeFOSE	87	6%
D9-NEtFOSE	76	10%
13C3-HFPO-DA	111	7%

Table 2. Average recoveries (%) and RSDs (%) for 24 surrogate PFAS in synthetic wastewater (1633).

Conclusion

40 native PFAS compounds were analyzed using EPA method 1633 (Table 1). All recoveries were 75% or higher with RSDs (%) all < 10%. The PFAS recoveries were within the acceptance windows (different for each compound) required by the method. Run time of the semi-automated system is < 70 min. Note that with method 1633 no final concentration step is required. The EZPFC produces very good recoveries with low standard deviations.

Surrogate PFAS recoveries (%) and RSDs (%) are shown in Table 2. Excellent data were obtained.

The semi-automated SPE system produces data that is as good as the more expensive fully automated SPE systems. The system is easy to operate and has only the vacuum pump as a mechanical part. Cleaning the system between runs is very quick and easy.

Note that that system has very low, mostly non-detect native background values for PFAS and cross-contamination risk is very low.

An important problem with ground and wastewater extraction is the presence of particulate matter which can easily plug up cartridges. Use of plastic filtration wool in the barrel of the cartridges can eliminate this problem. In this work no clogging of cartridges was observed.

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