Application Note

EPA Method 533 Analysis of Per- and Polyfluoroalkyl Substances in Drinking Water Using Semi-Automated Solid Phase Extraction (EZPFC®)

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a family of diverse, yet interrelated, synthetic compounds, first developed in the 1940s. PFAS are used in various products, ranging from Teflon to firefighting foams to food packaging. However, in recent years, these ubiquitous chemicals have been found to persist in groundwater and drinking water, due to their resistant molecular structure. Hence, they are classified as frontier pollutants, and the EPA has recently developed certain methods for their extraction and analysis. The extraction method outlines the use of solid phase extraction for drinking water matrix samples employing WAX cartridges.

Consistent with other EPA 500 series methods, EPA 533 incorporates a rigid set of QC and acceptance criteria requiring precise and reproducible analytical practices. The potential for error and the variability associated with manual extractions makes the benefits of semi-automating these processes apparent.

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 12-position EZ-PFC® System
- FMS SuperVap-24 PFC®
- Vacuum pump
- Agilent 6475 LCMS

Consumables

- FMS, Inc. 500 mg WAX PFC cartridge
- Ultra-pure DI water
- Fisher Pesticide Grade Methanol
- Acetic acid
- Ammonium acetate
- Sodium phosphate (monobasic and dibasic)
- Ammonium hydroxide
- Method 533 native and labeled spiking standards
- 15 mL polypropylene tubes

Procedure

- 12 samples (250 mL water each) are prepared, containing 1g/L ammonium acetate
- Acetic acid is used to adjust pH to ~6-8
- Spike with various 533 standards
- Cartridges are installed in each of the twelve positions.

Stage 1:

- Vacuum is turned on
- Cartridges are conditioned with 10 mL methanol (keep wet), 10 mL phosphate buffer (keep wet), and 3 mL phosphate buffer with 2 mL of water (keep wet)
- Samples are loaded across cartridges under vacuum, at 5 mL/min.
- Cartridges are rinsed with 10 mL 1 g/L ammonium acetate in water, then 1 mL methanol
- Cartridges are dried under nitrogen for 5 min

Stage 2:

- Methanol with 2% ammonium hydroxide is added to the rinse bottles (2 x 5 mL) and sprayed across the sample bottles.
- The 5 mL methanol aliquots are pulled drop wise across the cartridges and the eluent is collected.

FMS SuperVap®

- Pre-heat temp: 55-60 ºC
- Pre-heat time: 5 minutes
- Heat in Sensor mode at 55-60 ºC under nitrogen (5-7 psi)
- Direct to LC Vial Vessel Reduce to dryness and reconstitute to 1 mL as per method (20% water - 80 % methanol)
- Samples are now ready for analysis

FMS
Fluid Management Systems

Analysis

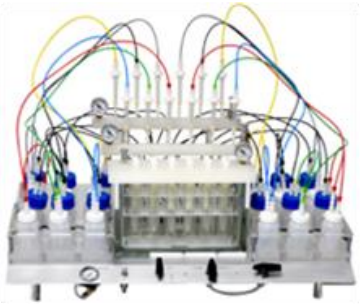
- Extract is 5 mL times 2, total 10 mL methanol (plus 2% ammonium hydroxide), then concentrated down to dryness. Add 1 mL (80/20) methanol-water.
- Agilent 1290 Infinity II LC System
- Agilent 6475 Triple quad LC/MS
- Agilent Zorbax Eclipse Plus C18 column 2.1 x 50 mm, 1.9 um
- Column temperature 50 °C
- Injection 10.0 uL
- Mobile phase 20 mM ammonium acetate in H_2O (A) and methanol (B)
- Gradient:

Time (min)	%A	%B
0	95	5
0.5	95	5
3.0	60	40
16.0	20	80
18.0	20	80
20.0	5	95

Dynamic MRM negative electrospray

- T (gas) = 230 °C
- T (sheath) = 375 °C

EZPFC SPE System



Name	EZPF-IDC-1 Final Conc.	EZPF-IDC-2 Final Conc.	EZPF-IDC-3 Final Conc.	EZPF-IDC-4 Final Conc.	EPA Window	RSD (%)
11Cl-PF3OUds	101.2	100.9	103.3	106.5	70-130	2.5
4-2FTS	117.3	105.4	116.1	101.7	70-130	7.0
6-2FTS	120.3	116.6	111.8	124.0	70-130	4.4
8-2FTS	81.4	78.9	89.8	81.4	70-130	5.7
9Cl-PF3OUds	100.1	94.5	99.5	97.5	70-130	2.6
ADONA	117.1	107.5	111.3	108.3	70-130	3.9
HFPO-DA	112.9	100.4	101.7	112.8	70-130	6.4
NFDHA	100.2	81.3	97.9	89.6	70-130	9.3
PFBA	118.3	124.2	120.5	127.3	70-130	3.3
PFBS	89.0	102.3	91.1	83.1	70-130	8.8
PFDA	88.0	79.6	83.1	97.2	70-130	8.8
PFDoA	84.1	78.5	75.7	84.7	70-130	5.4
PFEESA	83.7	82.0	87.1	84.7	70-130	2.5
PFHpA	107.2	105.4	108.7	102.8	70-130	2.4
PFHxA	95.0	107.1	93.9	91.4	70-130	7.2
PFHxS	84.9	90.0	92.9	88.8	70-130	3.7
PFMBA	100.2	81.3	97.9	89.6	70-130	9.3
PFMPA	77.5	80.7	80.9	79.7	70-130	2.0
PFNA	74.4	61.5	70.0	74.9	70-130	8.8
PFOA	105.3	87.5	92.6	85.0	70-130	9.7
PFOS	93.7	95.4	94.8	99.3	70-130	2.5
PFPeA	93.0	98.0	93.8	98.9	70-130	3.1
PFPeS	84.4	82.7	80.0	99.0	70-130	9.8
PFPpS	88.1	95.2	92.1	90.8	70-130	3.3
PFUdA	94.8	85.5	107.4	91.0	70-130	9.8

Table 1. Recoveries (%) and RSDs (%) for 25 native PFAS in drinking water (533) using EZPFC (spiked with 10 ng/L).

Name	EZPF-IDC-1 % Recoveries	EZPF-IDC-2 % Recoveries	EZPF-IDC-3 % Recoveries	EZPF-IDC-4 % Recoveries	EPA Window	RSD (%)
4-2FTS-13C2	103	121	129	130	50-200	10.4
6-2FTS-13C2	103	116	126	127	50-200	9.4
8-2FTS-13C2	104	90	78	87	50-200	12.0
HFPO-DA-13C3	73	69	70	61	50-200	7.7
PFBS-13C3	88	105	120	106	50-200	12.4
PFDA-13C6	82	111	93	100	50-200	12.7
PFDoA-13C2	113	113	91	101	50-200	10.3
PFHpA-13C4	75	90	91	99	50-200	11.4
PFHxA-13C5	92	100	98	77	50-200	11.3
PFHxS-13C3	119	139	123	139	50-200	8.2
PFNA-13C9	112	99	107	85	50-200	11.6
PFOA-13C8	101	101	112	111	50-200	5.6
PFOS-13C8	90	109	104	122	50-200	12.3
PFPeA-13C5	83	92	78	86	50-200	6.9
PFUdA-13C7	78	103	78	82	50-200	14.0
PFBA-13C4	105	104	102	101	50-200	1.6

Table 2. Recoveries (%) and RSDs (%) for 16 surrogate PFAS in drinking water (533) using EZPFC (spiked with 40-160 ng/L).

Name	EZPFC-MDL-1 Final Conc.	EZPFC-MDL-2 Final Conc.	EZPFC-MDL-3 Final Conc.	EZPFC-MDL-4 Final Conc.	EZPFC-MDL-5 Final Conc.	EZPFC-MDL-6 Final Conc.	EZPFC-MDL-7 Final Conc.	STDEV	MDL
11Cl-PF3OUds	1.07	1.13	1.07	1.11	1.09	1.09	1.01	0.04	0.11
4-2FTS	1.10	0.95	1.26	1.01	0.99	1.34	1.18	0.14	0.45
6-2FTS	0.92	0.92	0.71	0.97	0.96	0.98	1.21	0.15	0.46
8-2FTS	0.72	1.06	1.07	0.79	0.78	1.42	1.02	0.24	0.76
9Cl-PF3OUds	0.99	1.10	1.09	1.07	1.05	0.91	1.00	0.07	0.22
ADONA	1.20	1.01	1.11	1.17	1.15	1.24	1.17	0.07	0.23
HFPO-DA	1.12	1.16	1.43	0.93	0.91	1.02	0.76	0.21	0.67
NFDHA	1.07	1.10	1.01	0.99	0.97	0.97	1.00	0.05	0.16
PFBA	1.29	1.35	1.32	1.31	1.29	1.30	1.18	0.05	0.16
PFBS	0.66	1.50	0.74	0.81	0.79	0.71	0.89	0.29	0.90
PFDA	0.68	0.66	0.82	0.97	0.95	0.69	0.78	0.13	0.40
PFDoA	1.17	0.71	0.97	0.93	0.91	1.04	0.74	0.16	0.50
PFEESA	0.90	0.92	0.91	0.89	0.88	0.89	0.84	0.03	0.08
PFHpA	1.16	1.04	1.05	1.00	0.99	1.08	1.07	0.06	0.18
PFHxA	1.15	1.18	1.03	1.02	1.00	1.07	0.95	0.08	0.25
PFHxS	0.81	1.08	0.82	0.94	0.93	0.78	0.85	0.11	0.33
PFMBA	1.07	1.10	1.01	0.99	0.97	0.97	1.00	0.05	0.16
PFMPA	0.82	0.85	0.82	0.82	0.81	0.81	0.78	0.02	0.07
PFNA	0.64	0.94	0.74	0.88	0.86	0.70	0.75	0.11	0.34
PFOA	0.89	1.11	0.80	0.90	0.88	1.09	1.05	0.12	0.38
PFOS	1.02	1.04	1.04	0.99	0.97	0.94	0.94	0.04	0.14
PFPeA	0.95	1.07	1.03	1.04	1.02	0.95	0.93	0.05	0.17
PFPeS	1.41	0.93	1.20	0.94	0.92	0.98	0.85	0.20	0.62
PFPpS	1.00	1.16	1.32	1.00	0.98	0.65	0.88	0.21	0.66
PFUdA	0.89	0.77	1.02	1.06	1.04	1.05	0.95	0.10	0.33

Table 3. Method Detection Limit values (ng/L) for 25 native PFAS in drinking water (533) using EZPFC (spiked with 1.0 ng/L).

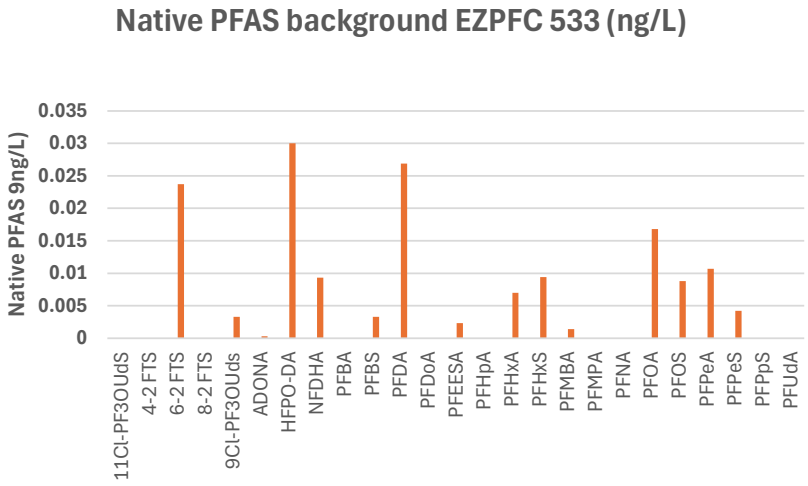


Figure 1. Native PFAS background with EZPFC for method 533 (in ng/L).

Discussion and Conclusions

Table 1 shows the Demonstration of Capability with the EZPFC system for method 533: all 25 native PFAS gave recoveries between 70-130 % (the method's acceptance window) with RSDs within 10%. These results show the dependability of the EZPFC as a simple semi-automated system that uses a vacuum pump as the only mechanical component.

Surrogate PFAS recoveries (%) and acceptance windows (%) are shown in Table 2. Excellent data were obtained for the sixteen surrogates well within those windows.

The Method Detection Limit study for these 25 native PFAS showed most MDL values were < 0.50 ng/L: further proof of the system's reproducibility and lack of chance of native background cross-contamination.

This observation was consistent with Figure 1 which demonstrated very low native background for the EZPFC: for all 25 compounds values found were < 0.03 ng/L.

The results of the drinking water samples confirmed the ability of the FMS EZPFC system to deliver accurate results with excellent reproducibility. The system is inexpensive and easy to use. It is a good alternative for laboratories that currently use manual techniques, liquid-liquid extractions and glass manifolds.

Especially the combination of 2 EZPFCs and a SuperVap-PFC-24 offers the opportunity to process 24 PFAS samples within a 2-3 hour timeframe.

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