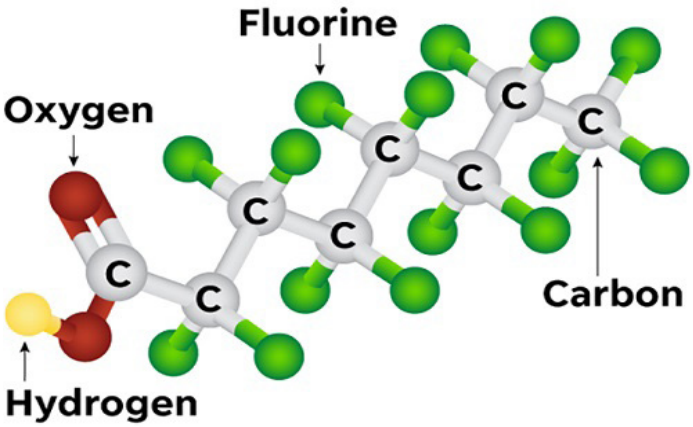
Per- and Polyfluoroalkyl Substances (PFASs) in Drinking Water Using Solid-Phase Extraction and LC-MS/MS



UCT Part Numbers

ECWAX126-P
ENVIRO-CLEAN® WAX
200 mg, 6 mL cartridge, PE frits

VMF016GL
16 position glass block manifold

SLC-18100ID21-3UM
Selectra® C18 HPLC column
(100 × 2.1 mm, 3 µm)

SLC-18GDC20-3UM
Selectra® C18 guard cartridge
(10 × 2.1 mm, 3 µm)

CLTTP050
Polypropylene Clean-Thru Tips

Summary:

This application note outlines a simple SPE procedure for the extraction of 26 diverseper- and polyfluoroalkyl substances (PFASs) in drinking water using UCT's polymeric weak-anion exchange SPE cartridges (ENVIRO-CLEAN® WAX). Instrumental analysis was carried out by LC-MS/MS in less than 10 minutes using a Selectra® C18 HPLC column. Overall, excellent recovery and reproducibility were obtained at the low concentrations tested.

Introduction:

Per- and polyfluoroalkyl substances (PFASs) are a diverse group of synthetic organofluorine compounds that have been widely used in industrial applications and consumer products such as non-stick cookware, food packaging, fire-fighting foams, carpeting, apparels and metal plating. PFASs are persistent in the environment and are extremely resistant to degradation due to heat, acids or bases. They are also bioaccumulative in wildlife and humans and are known to cause reproductive and developmental toxicity in laboratory animals and wildlife.

The United States Environmental Protection Agency (USEPA) has issued drinking water health advisories for two PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) at 70 ng/L [1]. Several US states also have public health guidelines for PFASs ranging from 20–7,000 ng/L in drinking water.

This study describes a method for the sensitive quantification of 26 PFASs in drinking water, including the 14 covered in the US EPA Method 537 [2]. In addition, fluorochemicals are present in polytetrafluoroethylene (PTFE) materials, so excluding the use of any PTFE labware throughout the sampling and analytical processes (including HPLC solvent inlet tubing) is essential for accurate analysis of PFASs. UCT's large volume sample transfer tubes allow for simplified sample preparation and are PTFE free, preventing any further introduction of contaminates to the samples.

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Sample Pretreatment:

To avoid any potential contamination with PFASs, water samples should not be collected in a fluorinated plastic container. Glass should also be avoided as it has been reported that certain PFASs can be retained on its surface. A polypropylene or polyethylene container is the most suitable option.

- Check the pH of the water sample to ensure that it is in the range of pH 6-8. If necessary, adjust pH using a small amount of 0.1M HCl or 0.1M NaOH (other suitable acids/bases can also be used).
- Spike sample with appropriate concentrations of surrogate standard and mix thoroughly (add target analytes for fortified samples)

SPE Procedure:

1. SPE conditioning

a) Rinse cartridge with 3mL methanol.
b) Rinse the cartridge with 5 mL of pH 7 buffer (0.1M acetate, formate or phosphate buffer), leaving approximately 2 mL of water on the top of the frit.

2. Sample extraction

a) Attach a large volume sample transfer tube to the top of each SPE cartridge and place the stainless-steel end of the transfer tube directly into the sample bottle.
*Ensure transfer tubes are adequately rinsed prior to use.
b) Adjust the vacuum so that the flow rate is approximately 5 mL/min.
c) After the sample is applied to the SPE cartridge, dry the cartridge under high vacuum (10-15 inHg) for 5 minutes to remove any residual water.

3. Elution

a) Insert a 15 mL polypropylene tube into the extraction manifold.
b) Add 6 mL of methanol containing 1% NH_4OH to the sample container.
Note: due to the volatility of NH_4OH, it is highly recommended to use fresh elution solvent.
c) Cap the sample container and thoroughly rinse the sides with the elution solvent.
Note: rinsing the sides of the container is important for obtaining good recovery of the longchain hydrophobic PFASs.
d) Apply a low vacuum to draw the elution solvent through the large volume sample transfer tubes and onto the SPE sorbent. Continue to elute the PFASs in a fast dropwise fashion.
e) After the solvent has passed through, apply full vacuum for 30 seconds so that all the elution solvent is collected.

4. Concentration

a) For samples spiked at 100 ppt (0.1 µg/L), the extract was evaporated to 5 mL.
b) For samples spiked at 10 ppt (0.01 µg/L), the extract was evaporated down to 1 mL.
Note: the extract can be evaporated to 0.5 mL in order to achieve better sensitivity (lower MDL); however, longer evaporation may result in lower recovery for some of the volatile analytes.
c) Add IS.
d) Vortex the samples and transfer 500 µL to a propylene HPLC vial (PTFE free).

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LC-MS/MS Parameters:

PFASs are ubiquitous in the laboratory environment, mainly through the widespread use of TeflonTM components in analytical equipment, including HPLC. In order to avoid high background in LC-MS/MS analysis, the TeflonTM solvent lines should be replaced with PEEK tubing. However, PFAS contamination is difficult to completely eliminate and depending on the analytical conditions used, any PFAS present in the mobile phase, solvent lines and online degasser can become concentrated in the analytical column and be detected at the same time as the injected sample analyte. To overcome this, a short C18 "delay column" is commonly installed after the solvent mixer and before the sample injector to separate the contaminant peak from any PFAS present in the sample. Alterations to existing HPLC systems can be readily performed, although it is recommended to check with your HPLC's vendor before proceeding [3]

Instrumentation	
MS/MS system	Shimadzu LCMS-8050
Ionization mode	ESI
HPLC system	Shimadzu Nexara X2
Delay column	UCT Selectra® C18, 50 × 4.6 mm, 5 µm (p/n: SLC-1850ID46-5UM)
HPLC column	UCT Selectra® C18, 100 × 2.1 mm, 3 µm (p/n: SLC-18100ID21-3UM)
Guard column	UCT Selectra® C18, 10 × 2.0 mm, 3 µm (p/n: SLC-18GDC20-3UM)
Guard column holder	p/n: SLGRDHLDR
Column temperature	45°C
Flow rate	300 µL/min
Injection volume	5 µL

Time (min)	Mobile Phase A (%) 10 mM Ammonium Formate	Mobile Phase B (%) Acetonitrile
0.0	90	10
0.5	65	35
5.0	5	95
6.0	5	95
6.1	90	10
10.0	90	10

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MRM Transitions:

#	Analyte	Acronym	Precursor Ion	Fragment Ion 1	Fragment Ion 2
	Perfluoroalkylcarboxylic acids (PFCAs)				
1	Perfluorobutanoic acid	PFBA	213.0	169.1	N/A
2	Perfluoropentanoic acid	PFPeA	263.0	219.0	141.1
3	Perfluorohexanoic acid	PFHxA	313.0	269.1	118.9
4	Perlfuoroheptanoic acid	PFHpA	362.8	319.1	169.1
5	Perfluorooctanoic acid	PFOA	412.8	369.1	169.2
6	Perfluorononanoic acid	PFNA	463.1	419.0	219.2
7	Perfluorodecanoic acid	PFDA	513.1	468.9	219.1
8	Perfluoroundecanoic acid	PFUdA	563.1	518.9	268.8
9	Perfluorododecanoic acid	PFDoA	612.9	569.0	319.1
10	Perfluorotridecanoic acid	PFTrDA	662.9	618.9	169.2
11	Perfluorotetradecanoic acid	PFTeDA	713.0	668.9	169.1
	Perfluoroalkanesulfonates (PFASs)				
12	Potassium perfluoro-1-butanesulfonate	PFBS	299.0	79.9	99.0
13	Sodium perfluoro-1-pentanesulfonate	PFPeS	349.0	80.0	99.1
14	Potassium perfluorohexanesulfonate	PFHxS	399.0	80.0	99.0
15	Sodium perfluoro-1-heptanesulfonate	PFHpS	449.1	80.0	99.1
16	Potassium perfluorooctanesulfonate	PFOS	499.1	80.0	99.0
17	Sodium perfluoro-1-nonanesulfonate	PFNS	548.9	80.0	99.1
18	Sodium perfluoro-1-decanesulfonate	PFDS	598.9	80.0	99.1
	Perfluorooctanesulfonamides (FOSAs)				
19	Perfluorooctane sulfonamide	FOSA	498.1	78.0	477.9
	Fluorotelomer sulfonates (FTSs)				
20	Sodium 1H,1H,2H,2H-perfluoro-1-hexanesulfonate	4:2 FTS	327.0	307.1	81.0
21	Sodium 1H,1H,2H,2H-perfluoro-1-octanesulfonate	6:2 FTS	427.1	407.0	81.0
22	Sodium 1H,1H,2H,2H-perfluoro-1-decanesulfonate	8:2 FTS	527.1	506.8	81.0
	Perfluorooctanesulfonamidoacetic acids (FOSAAs)				
23	Perfluorooctanesulfonamidoacetic acid	FOSAA	556.1	497.9	419.0
24	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	569.7	418.9	482.9
25	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	584.1	419.1	526.1
	Perfluoroalkylphosphonic acids (PFPAs)				
26	Perfluorohexane phosphonic acid	PFHxPA	399.0	79.0	339.2
	Internal Standards				
IS 1	Perfluoro-n-[2,3,4-$^{13}C_3$]butanoic acid	M3PFBA	216.1	172.1	N/A
IS 2	Perfluoro-n-[2,3,4-$^{13}C_3$]hexanoic acid	MPFHxA	315.0	270.1	120.1
IS 3	Perfluoro-n-[1,2-$^{13}C_2$]octanoic acid	M2PFOA	415.0	370.0	169.1
IS 4	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	MPFDA	514.9	469.9	220.1
IS 5	N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid	d5-NEtFOSAA	588.9	419.0	530.9
IS 6	Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	MPFOS	502.9	80.0	99.0

Note: All standards were purchased in liquid form from Wellington Laboratories LLC. (Overland Park, KS, U.S.A.)

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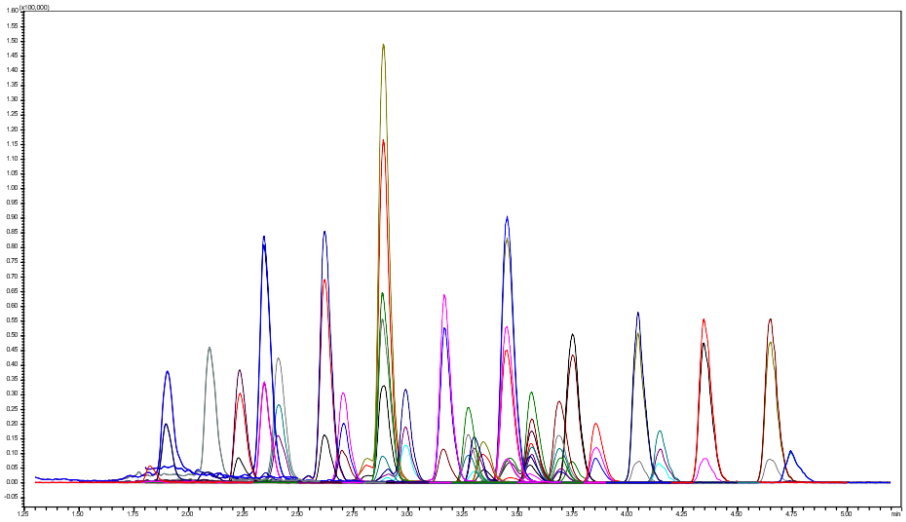

Figure 1: PFASs fortified at 10 ppt (0.01 µg/L) in tap water

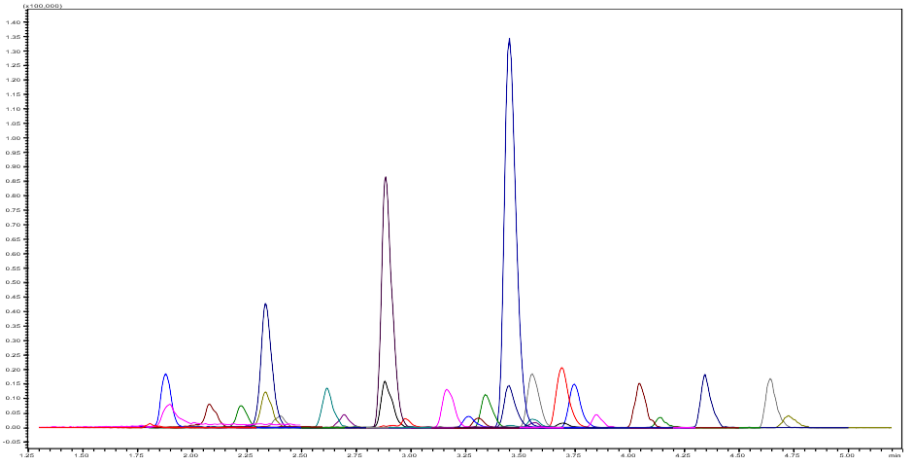

Figure 2: PFASs 0.5 ppb standard

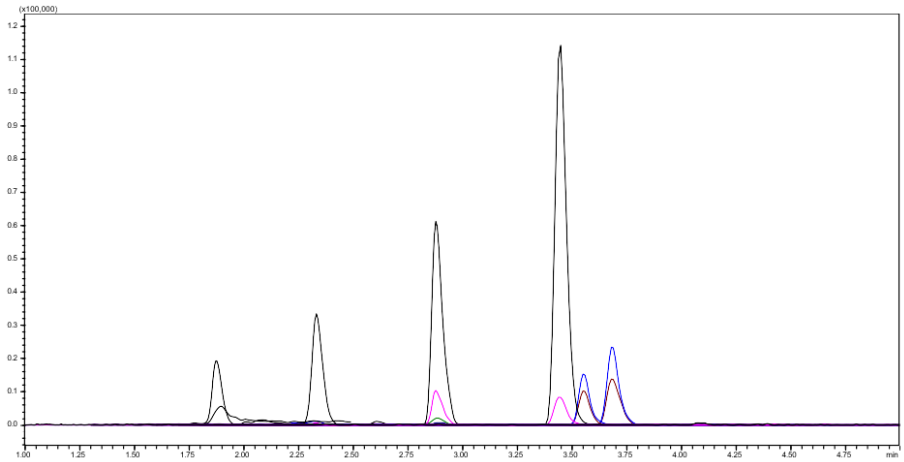

Figure 3: Laboratory reagent blank (LRB) with IS

Retention Times:

Analyte	RT (min)	IS Group	Calibration Curve Range (µg/L)	R^2
PFBA	1.89	1	0.5 - 10	0.9867
PFPeA	2.08	1	0.5 - 10	0.9995
PFHxPA	1.80	1	0.5 - 10	0.9960
PFBS	2.40	6	0.5 - 10	0.9998
4:2 FTS	2.23	6	0.5 - 10	0.9990
PFHxA	2.33	2	0.5 - 10	0.9994
PFPeS	2.69	6	0.5 - 10	0.9976
PFHpA	2.61	2	0.5 - 10	0.9981
PFHxS	2.97	6	0.5 - 10	0.9992
PFOA	2.88	3	0.5 - 10	0.9974
6:2 FTS	2.76	6	0.5 - 10	0.9952
PFHpS	3.30	6	0.5 - 10	0.9991
PFNA	3.18	3	0.5 - 10	0.9968
PFOS	3.58	6	0.5 - 10	0.9995
PFNS	3.96	6	0.5 - 10	0.9989
PFDA	3.46	4	0.5 - 10	0.9998
8:2 FTS	3.33	6	0.5 - 10	0.9992
FOSAA	3.36	5	0.5 - 10	0.9937
PFDS	4.16	6	0.5 - 10	0.9978
PFUdA	3.76	4	0.5 - 10	0.9994
N-MeFOSAA	3.57	5	0.5 - 10	0.9947
N-EtFOSAA	3.72	5	0.5 - 10	0.9962
PFDoA	4.07	4	0.5 - 10	0.9979
PFTrDA	4.37	4	0.5 - 10	0.9981
FOSA	4.77	5	0.5 - 10	0.9999
PFTeDA	4.66	4	0.5 - 10	0.9999
Internal Standards				
M3PFBA	1.86	IS 1	4	N/A
MPFHxA	2.33	IS 2	2	N/A
M2PFOA	2.90	IS 3	4	N/A
MPFDA	3.48	IS 4	6	N/A
d5-NEtFOSAA	3.72	IS 5	8	N/A
MPFOS	3.57	IS 6	4	N/A

Note: Calibration curve concentrations = 0.5, 1, 2, 5 and 10 µg/L.

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SPE Results:

	Deionized Water (n=4)				Tap Water (n=4)			
	Fortified conc = 10 ppt (0.01 µg/L)		Fortified conc = 100 ppt (0.1 µg/L)		Fortified conc = 10 ppt (0.01 µg/L)		Fortified conc = 100 ppt (0.1 µg/L)	
Analyte	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
PFBA	121	10.6	123	7.5	105	16.6	107	11.9
PFPeA	112	2.9	110	5.6	102	14.5	92	9.8
PFHxA	103	5.8	103	6.5	109	7.6	105	7.9
PFHpA	101	5.9	105	4.9	99	5.1	99	6.1
PFOA	99	6.9	98	5.0	114	9.3	99	8.7
PFNA	104	5.4	108	8.1	100	9.8	94	10.7
PFDA	104	6.3	98	3.4	107	1.9	96	5.6
PFUdA	101	7.5	87	4.3	95	5.3	89	6.5
PFDoA	97	6.2	99	3.3	104	9.4	93	4.1
PFTrDA	105	5.7	102	5.7	100	12.6	93	7.8
PFTeDA	95	2.1	100	6.2	98	13.9	92	7.2
PFBS	108	5.2	110	5.0	99	8.3	93	5.1
PFPeS	99	8.3	100	4.1	96	9.6	93	5.7
PFHxS	91	12.6	98	5.9	105	14.4	100	7.8
PFHpS	91	8.3	90	4.7	86	8.9	84	6.4
PFOS	91	14.5	90	2.8	90	10.6	87	2.2
PFNS	96	5.9	97	5.2	84	6.7	86	5.5
PFDS	97	3.9	93	3.4	94	10.1	84	6.7
FOSA	90	4.4	96	7.1	82	6.3	84	12.6
N-MeFOSAA	105	6.5	96	10.8	90	7.7	97	9.0
N-EtFOSAA	100	8.6	87	19.8	99	6.1	101	3.8
FOSAA*	64	13.5	58	0.9	30	33.6	30	23.7
PFHxPA	102	10.4	106	7.3	87	10.2	91	8.9
4:2 FTS	111	5.4	108	5.7	83	6.1	85	6.2
6:2 FTS**	158	65.1	211	66.0	214	107.9	77	5.4
8:2 FTS	113	4.5	105	9.9	102	6.8	84	5.3

Note: A 250 mL water sample fortified at 10 ppt (0.01 µg/L) gives a final concentration (after SPE and evaporation to 1 mL) of 2.5 µg/L.

A 250 mL water sample fortified at 100 ppt (0.1 µg/L) gives a final concentration (after SPE and evaporation to 5 mL) of 5 µg/L.

** Low Recovery of FOSAA due to potential loss during evaporation.*

*** High Recovery of 6:2 FTS due to potential exogenous contamination.*

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Conclusion:

This application note outlines a simple SPE method for the determination of a wide range of PFASs in drinking water using LC-MS/MS with a Selectra® C18 column. The results indicate that UCT's polymeric weak-anion exchange SPE cartridges (ENVIRO-CLEAN® WAX) can be used to simultaneously extract 26 PFASs in drinking water at environmentally relevant concentrations. All PFASs were quantified with good linearity of calibration using 6 mass-labelled internal standards. The recovery and RSD values obtained were within the acceptance criteria of the EPA method 537. The method can also be used as a starting point for a custom method that is tailored to a specific matrix or additional compounds. In this case, further optimization of the method can be carried out to optimize results. Precautions must be taken to ensure all components a sample may come in contact with during the extraction process and analysis from start to finish are void of PTFE.

References:

[1] Unregulated Contaminant Monitoring Rule 3 (UCMR3), accessed online November 2017, http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/

[2] 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, September 2009, EPA/600/R-08/092.

[3] Shimadzu's Parts Compatibility Guide for LCMS Analysis of PFC's; accessed from Shimadzu website on November 2017; http://www.ssi.shimadzu.com/products/literature/lcms/085_Shimadzu%E2%80%99s%20Guide%20to%20US%20DOD_DOE%20Analysis%20of%20PFCs%20using%20the%20LCMS-8060.pdf.

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