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Determination of per- and polyfluorinated alkyl substances (PFAS) in drinking water using automated solid-phase extraction and LC-MS/MS

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INTRODUCTION

Per- and polyfluorinated alkyl substances (PFAS) are a group of man-made chemicals including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and GenX chemicals that have been manufactured and used in a variety of industries globally.[1,2] These compounds have a wide range of commercial product applications including industrial polymers, stain repellents, surfactants, waterproofing products, packaging, and aqueous film forming foams used for firefighting. PFAS are highly soluble in water, chemically stable, persistent in the environment, and can accumulate in the human body over time, leading to adverse human health effects.[3]

In November 2018, the United States Environmental Protection Agency (U.S. EPA) published Method 537.1 "Determination of selected per- and polyfluorinated alkyl substances in drinking water by solid phase extraction and LC/MS/MS".[4] The method uses an offline solid-phase extraction (SPE) with liquid chromatography tandem mass spectrometry (LC-MS/MS) to extract, enrich, and determine 18 PFAS in drinking water. Currently most testing laboratories perform the sample extraction manually using a vacuum manifold, which is labor-intensive, time consuming, and the flow rate through the cartridge is difficult to control. There is a high demand for automation of the SPE procedure.

In this poster, we discuss the development of an analytical method using an automated SPE system, AutoTrace 280, and LC-MS/MS for determination of eighteen PFAS following the guidelines provided by U.S. EPA Method 537.1. We have demonstrated that the AutoTrace 280 system provides reliable automated SPE for determination of PFAS in large-volume (20 mL–4 L) aqueous samples.

MATERIALS AND METHODS

Equipment

- Thermo Scientific™ Dionex™ AutoTrace 280 PFAS™ System (1)
- Thermo Scientific™ Vanquish™ Flex Duo UHPLC system, fitted with Thermo Scientific™ PFC free kit (2)
- Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer (3)
- Organomation Associates™ 12 Position N-EVAP Nitrogen Evaporator (4)

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Method Workflow

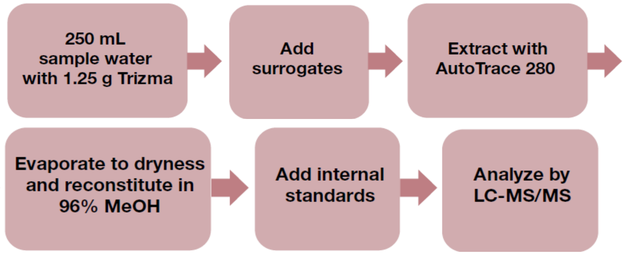

Figure 1. U.S. EPA Method 537.1 procedure workflow

Table 1 . Cartridge Conditioning and Sample Loading (program this method in solid-phase extraction mode)

No.	Method (programmed)	User intervention/information
1	Process six samples using the following method steps	
2	Condition cartridge with 7.5 mL of MeOH into solvent waste	
3	Condition cartridge with 7.5 mL of MeOH into solvent waste	
4	Condition cartridge with 9.0 mL of water into aqueous waste	
5	Condition cartridge with 9.0 mL of water into aqueous waste	
6	Load 270.0 mL of sample onto cartridge	Sample bottle actually contains 250 mL of sample. The method is programmed to deliver 270 mL sample as it accounts for the delay volume in the system. Waste automatically goes to aqueous waste.
7	Pause and Alert operator, resume when CONTinue is pressed	Add 7.5 mL reagent water into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into sample.
8	Load 17.5 mL of sample onto cartridge	The method is programmed to consider the delay volume
9	Pause and Alert operator, resume when CONTinue is pressed	Add 7.5 mL water into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into sample.
10	Load 21.5 mL of sample onto cartridge	The method is programmed to consider the delay volume and to pull all the aqueous phase from the tubes.
11	Dry cartridge with gas for 10.0 minutes	
12	End	

Step	Flow rate (mL/min)
Cond flow	10.0
Load flow	10.0
Rinse flow	10.0
Elute Flow	1.0
Cond air push	15.0
Rinse air push	20.0
Elute air push	5.0

SPE parameters	
Push delay	5 s
Air factor	1.0
Autowash vol.	1.0 mL

Instrument parameters	
Max elution vol.	20.0 mL
Exhaust fan on	Yes
Beeper on	Yes

Table 2. Sample Elution (program this method in solid-phase elute mode)

No.	Method (programmed)	User intervention/information
		This step must be performed before pressing CONTinue on the front panel. Add 4.0 mL methanol into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into that 4 mL methanol.
1	Process six samples using the following method steps	
2	Manually rinse sample container with 14.0 mL to collect	First, elute with 4.0 mL MeOH. The method is programmed to consider the delay volume.
3	Pause and alert operator, resume when CONTinue is pressed	Add 4.0 mL methanol into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into that 4 mL methanol.
4	Manually rinse sample container with 18.0 mL to collect	Second, elute with 4.0 mL MeOH. The method is programmed to consider the delay volume and push out any residual methanol.
5	End	

Step	Flow rate (mL/min)
Cond flow	1.0
Load flow	1.0
Rinse flow	1.0
Elute flow	1.0
Cond air push	15.0
Rinse air push	20.0
Elute air push	5.0

SPE parameters	
Push delay	5 s
Air factor	1.0
Autowash vol.	1.0 mL

Instrument parameters	
Max elution vol.	20.0 mL
Exhaust fan on	Yes
Beeper on	Yes

*Do not detach the cartridges during methods one and two

Table 3. LC conditions and MS parameters

Parameter	Value
Analytical column	Accucore RP-MS, 2.1 × 100 mm, 2.6 µm
Isolator column	Hypersil BDS C18, 2.1 × 50 mm, 5 µm. This column was installed prior to the autosampler to remove any contaminants from the mobile phase.
Column temp.	45 °C
Flow rate	0.5 mL/min
Injection volume	5 µL
Autosampler temp.	6 °C
Solvent A	Water containing 0.1% acetic acid
Solvent B	Methanol containing 0.1% acetic acid
Solvent C	20 mM ammonium acetate in water
Gradient	Time (min) %B %C 0 30 5 1 30 5 14 95 5 17 95 5 18 30 5 21 30 5

Parameter	Value
Ion source type	H-ESI
Polarity	Negative
Negative ion	2500 V
Sheath gas	50 arbitrary units
Aux gas	10 arbitrary units
Sweep gas	1 arbitrary units
Ion transfer tube temp.	325 °C
Vaporizer temp.	300 °C
Q1 resolution (FWHM*)	0.7
Q3 resolution (FWHM*)	1.2
CID gas	2 mTorr

*FWHM: Full width at half maximum

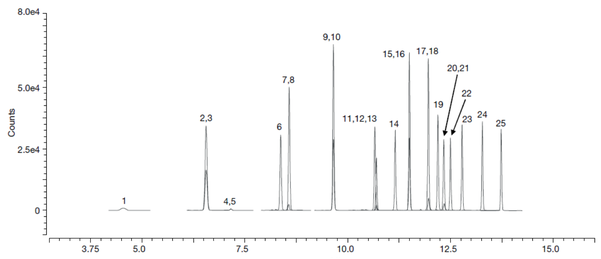

Figure 2. LC-MS/MS chromatograms of PFAS at 4 µg/L standard solution

Table 4. Retention time, asymmetry factor, and internal standards for method PFAS

Peak No.	Peak Name	Retention Time (min)	Asymmetry Factor	IS # ref
1	PFBS	4.56	1.09	$^{13}C_4$-PFOS
2	PFHxA	6.56	1.01	$^{13}C_2$-PFOA
3	$^{13}C_2$-PFHxA	6.56	0.96	$^{13}C_2$-PFOA
4	HFPO-DA	7.16	0.84	$^{13}C_2$-PFOA
5	^{13}C-HFPO-DA	7.16	0.84	$^{13}C_2$-PFOA
6	PFHpA	8.37	1.01	$^{13}C_2$-PFOA
7	ADONA	8.57	1.12	$^{13}C_4$-PFOS
8	PFHxS	8.58	0.95	$^{13}C_2$-PFOA
9	PFOA	9.65	1.06	$^{13}C_2$-PFOA
10	$^{13}C_2$-PFOA	9.66	0.98	--
11	PFNA	10.66	0.99	$^{13}C_2$-PFOA
12	PFOS	10.70	1.03	$^{13}C_4$-PFOS
13	$^{13}C_4$-PFOS	10.70	1.04	--
14	9Cl-PF3ONS	11.16	1.16	$^{13}C_4$-PFOS
15	PFDA	11.50	1.03	$^{13}C_2$-PFOA
16	$^{13}C_2$-PFDA	11.50	0.95	$^{13}C_2$-PFOA
17	NMeFOSAA	11.96	1.08	--
18	d_3-NMeFOSAA	11.97	1.05	d_3-NMeFOSAA
19	PFUnA	12.19	1.00	$^{13}C_2$-PFOA
20	NEtFOSAA	12.34	0.93	$^{13}C_2$-PFOA
21	d_5-NEtFOSAA	12.35	1.10	d_3-NMeFOSAA
22	11Cl-PF3OUdS	12.50	1.05	$^{13}C_4$-PFOS
23	PFDoA	12.78	1.07	$^{13}C_2$-PFOA
24	PFTrDA	13.27	1.01	$^{13}C_2$-PFOA
25	PFTA	13.70	0.94	$^{13}C_2$-PFOA

Table 5. Precision and accuracy (n=6) of PFAS in fortified drinking water

Analyte	Fortified conc. (ng/L)	Mean recovery (%)	RSD (%)	Fortified conc. (ng/L)	Mean recovery (%)	RSD (%)
PFBS	16.0	107	3.3	80.0	98.3	3.6
PFHxA	16.0	108	2.3	80.0	106	2.6
HFPO-DA	16.0	84.1	7.5	80.0	88.6	6.3
PFHpA	16.0	113	2.7	80.0	117	1.3
PFHxS	16.0	120	3.4	80.0	123	2.1
ADONA	16.0	117	2.5	80.0	121	1.1
PFOA	16.0	113	2.5	80.0	119	1.6
PFNA	16.0	114	2.9	80.0	118	2.1
PFOS	16.0	113	4.5	80.0	117	2.9
9Cl-PF3ONS	16.0	96.1	4.1	80.0	103	2.6
PFDA	16.0	105	3.2	80.0	111	2.1
PFUnA	16.0	96.8	5.0	80.0	103	3.1
NMeFOSAA	16.0	103	5.2	80.0	110	5.2
11Cl-PF3OUdS	16.0	88.5	5.5	80.0	97.1	4.8
NEtFOSAA	16.0	100	9.9	80.0	104	2.3
PFDoA	16.0	89.8	4.4	80.0	97.3	3.4
PFTrA	16.0	89.6	3.8	80.0	95.8	3.7
PFTA	16.0	89.0	4.8	80.0	98.1	3.3

CONCLUSIONS

This application note reports a method that can be used for the extraction and determination of 18 PFAS in drinking water with a PFAS-safe AutoTrace 280 extraction system and LC-MS/MS. The modified AutoTrace 280 extraction system ensures inertness and prevents PFAS from leaching into sample during extraction, while at same time delivering consistent and reliable performance. Both sample path cleaning in SPE and separation method precaution for the LC system maintained a low system background, meeting the EPA method requirement. The calculated LCMRLs ranged from 0.20 to 3.5 ng/L and the MDLs ranged from 0.30 to 2.5 ng/L, which were below or comparable to those values reported in U.S. EPA Method 537.1. At both 16.0 ng/L and 80.0 ng/L fortified concentration levels, all the recoveries were within the acceptable range of 70–130%. The calculated RSDs were all less than 10%, suggesting good precision. Thermo Scientific LC-MS/MS with the automatic extraction AutoTrace 280 system demonstrated an efficient, reliable, and sensitive method to fulfill the requirements of U.S. EPA Method 537.1.

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TRADEMARKS/LICENSING

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