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Ultra-fast Trace Quantitation of PFAS in Drinking and Environmental Waters Using an Automated Sample Preparation and LC-MS/MS System

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Overview and Introduction

As PFAS are highly stable, resistant to degradation and potentially harmful to humans, their presence and persistence in the environment have raised serious concerns globally. Common testing methods consist of manual SPE or direct injection into LC-MS/MS. With the increased need for trace-level (ppt) detection and high throughput methods, this study aims to achieve:

- Automated sample preparation with a small sample volume requirement (10 mL)
- Ultra-fast analysis of 62 PFAS compounds
- High-sensitivity analysis (detection limit of low ppt range) using LC-MS/MS

Methods

Sample Preparation

62 PFAS (including targets, IS and isotopically-labeled surrogates) were prepared using Biotage® Evolute® Express Sorbent Selection 30 mg Fixed Well Plate, WAX and an automated SPE system, Extrahera™.

Biotage® Extrahera™

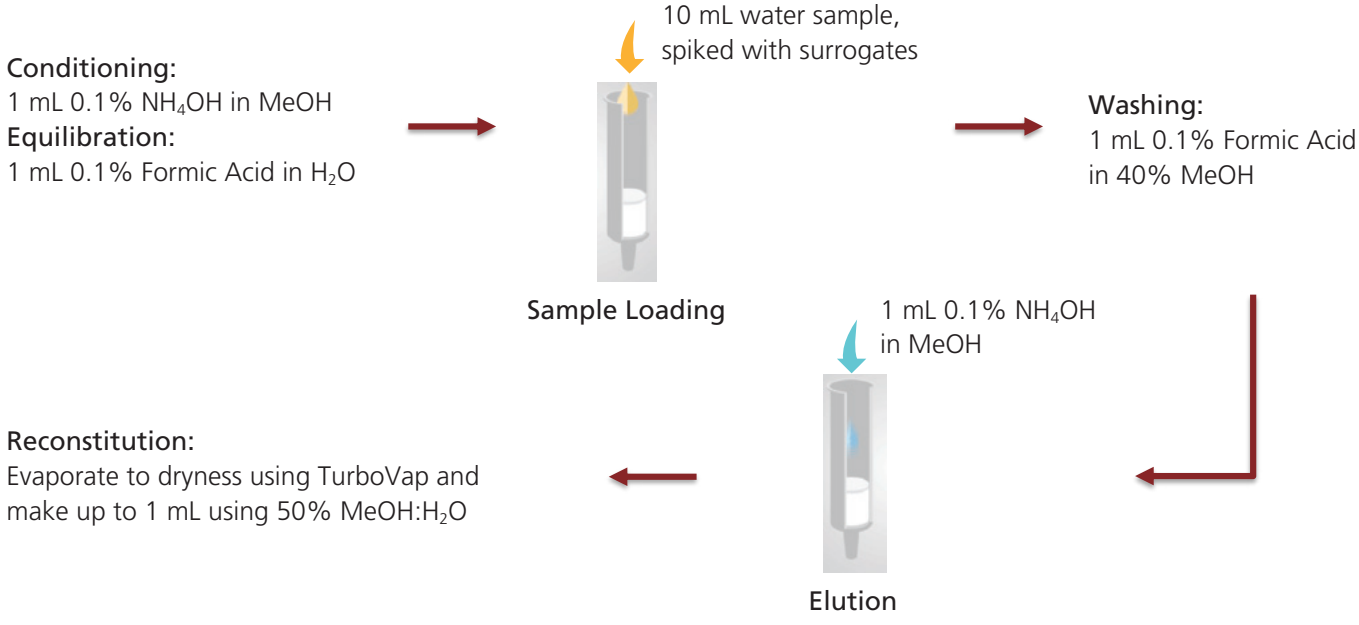

Figure 1. Sample preparation workflow

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Analytical Method and Instrument Conditions

250 µL of the prepared solution were directly injected into Shimadzu Nexera X2 UHPLC and Triple Quadrupole LCMS-8060 system. A delay column was used to account for the PFAS contamination present in the system and to ensure accurate determination of trace-level PFAS from the samples. The LCMS methods and list of PFAS are tabulated in Table 1 and 2.

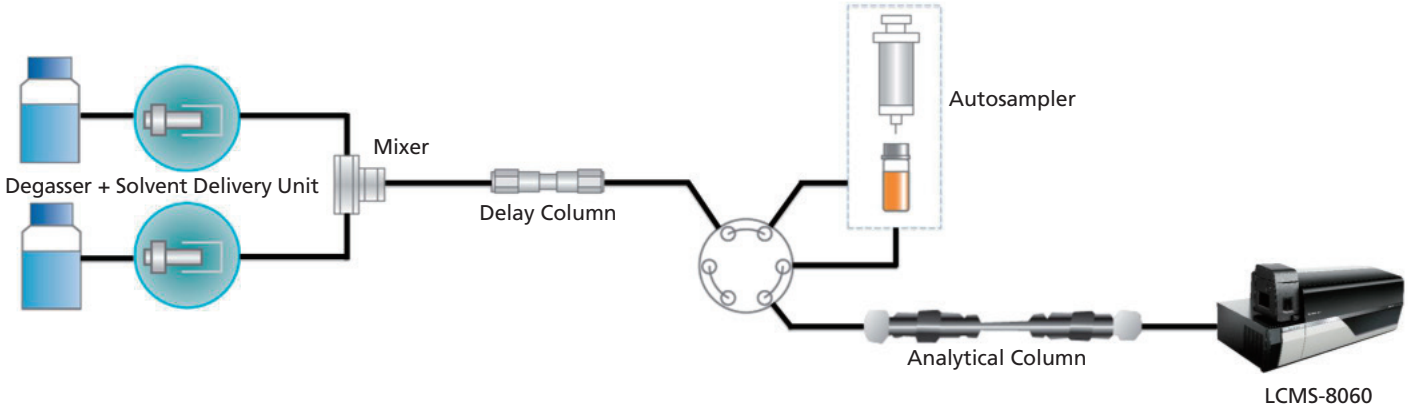

Figure 2. Setup of delay and analytical column in LCMS

Results

Chromatographic Separation

All 62 PFAS compounds were separated in a 7-minute LC-MS/MS run (Figure 3). Branched and structural isomers of PFHxS and PFOS (Figure 4) were chromatographically separated and excellent peak shapes were obtained for all compounds, including early-eluting components such as PFBA.

Table 1. UHPLC Conditions (Nexera X2 Binary UHPLC System)

Analytical Column	: Shim-pack™ ODS III, 2.0 mm x 50 mm, 1.6 µm particle size
Delay Column	: Shim-pack™ XR-ODS, 3.0 mm x 30 mm, 2.2 µm particle size
Mobile Phases	: A: Buffer B: Methanol (MeOH)
Flow Rate	: 0.4 mL/min
Gradient Elution	:

Time (minutes)	Concentration of B (%)
0.00	50
0.01 – 5.00	100
5.01 – 7.00	100

Injection Volume	: 250 µL
Column Temp.	: 40 °C

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Table 2. MS Conditions (LCMS-8060)

Ionization: Heated ESI source, Negative (-), MRM Mode					
No.	Compound	MRM transition	No.	Compound	MRM transition
1	PFBA	212.70>169.20	32	d3–N–MeFOSAA	572.80>418.80
2	M3PFBA	216.40>172.15	33	FOSA	498.50>77.90
3	MPFBA	216.80>172.10	34	M8FOSA	505.80>172.00
4	M5PFPeA	268.30>223.15	35	PFDS	598.80>80.00
5	PFPeA	262.75>219.10	36	PFUdA	562.80>518.90
6	M3PFBS	301.80>80.05	37	d5–N–EtFOSAA	588.80>418.85
7	PFBS	298.80>79.90	38	N–EtFOSAA	584.20>526.00
8	4:2FTS	326.60>307.05	39	MPFDoA	614.80>569.80
9	M2–4:2FTS	328.90>308.90	40	PFDoA	612.75>568.70
10	PFHxA	312.90>269.00	41	M7PFUdA	569.80>524.90
11	M5PFHxA	318.40>273.00	42	10:2FTS	626.80>606.95
12	PFPeS	349.00>80.05	43	d7–N–MeFOSE–M	622.80>59.10
13	PFHpA	363.00>318.90	44	N–MeFOSE–M	616.50>59.20
14	M4PFHpA	366.90>321.90	45	d–N-MeFOSA–M	514.80>494.85
15	PFHxS	398.80>80.00	46	N–MeFOSA–M	512.00>169.20
16	6:2FTS	426.80>406.90	47	MFOUEA	459.00>393.85
17	M2–6:2FTS	429.00>408.85	48	M3PFHxS	401.80>79.90
18	PFOA	413.00>369.10	49	d9–N–EtFOSE–M	578.80>142.20
19	M8PFOA	420.90>375.95	50	PFTrDA	662.70>618.70
20	M2PFOA	415.00>369.90	51	N–EtFOSE–M	629.60>59.10
21	PFHpS	448.80>80.05	52	N–EtFOSA–M	526.50>169.00
22	M8PFOS	506.80>79.90	53	d–N–EtFOSA–M	530.80>168.90
23	PFNA	462.80>418.90	54	PFTeDA	713.00>669.00
24	MPFOS	502.80>79.95	55	M2PFTeDA	714.70>669.85
25	PFOS	499.00>80.00	56	M9PFNA	471.80>426.90
26	MPFDA	514.90>469.80	57	M2PFHxDA	814.70>769.70
27	M2–8:2FTS	528.80>508.85	58	PFHxDA	812.70>768.80
28	M6PFDA	518.80>473.85	59	FOUEA	456.80>392.90
29	8:2FTS	526.80>506.80	60	PFNS	548.70>80.00
30	PFDA	512.80>468.90	61	PFODA	912.60>868.70
31	N–MeFOSAA	569.80>419.00	62	8:2diPAP	988.60>542.85

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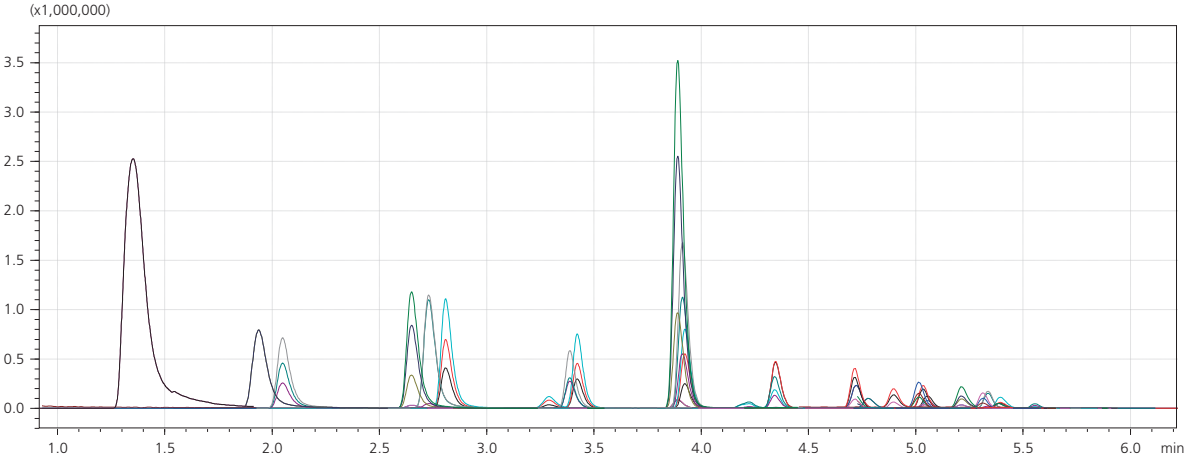

Figure 3. TIC and MRM chromatograms of 62 PFAS in a mixed standard solution (each conc. at 0.1 ppb)

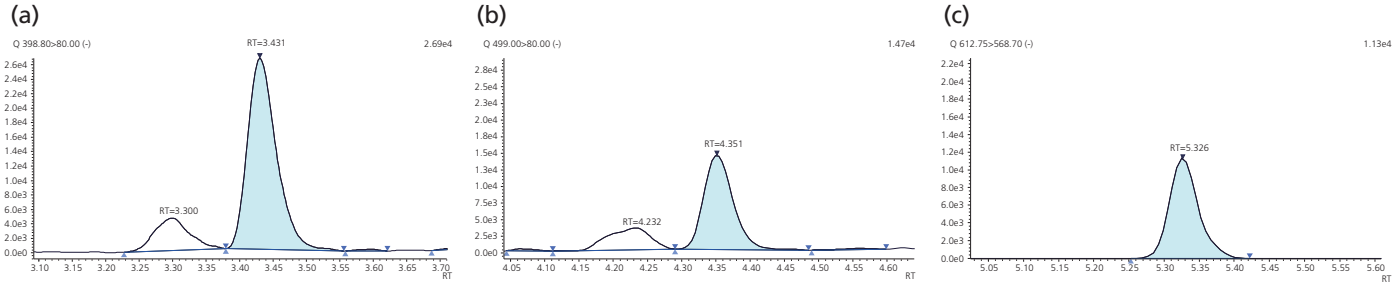

Figure 4. Separation of linear and branched isomers of (a) PFHxS and (b) PFOS, and (c) individual chromatogram of PFDoA, each at 0.005 ppb

Retention Time, Calibration Curve and Linearity

Table 3. Linearity and Sensitivity of Some PFAS Compounds*

Compound	RT (mins)	Linear Range (ppb)	Calibration Curve	R^2
PFBA	1.359	0.001 – 1	Y= 157879500X + 1578536	0.9990095
PFPeA	1.946	0.0005 – 1	Y= 36652110X + 12513.57	0.9994473
PFBS	2.058	0.0005 – 1	Y = 20873340X + 4041.694	0.9992726
4:2FTS	2.661	0.001 – 1	Y = 29330320X + 55976.77	0.9954744
PFHxA	2.741	0.0005 – 1	Y = 40942030X + 17406.84	0.9987026
PFPeS	2.821	0.0005 – 1	Y = 25081810X + 7401.714	0.9982985
PFHpA	3.401	0.001 – 1	Y = 8821824X + 24224.42	0.9955069
PFHxS	3.436	0.0005 – 1	Y = 15581750X + 3357.118	0.9995215
6:2FTS	3.904	0.01 – 1	Y = 11680710X + 7448587	0.9884024
PFOA	3.927	0.0005 – 1	Y = 34609260X + 33462.22	0.9922736
PFHpS	3.938	0.0005 – 1	Y = 18344270X + 6004.611	0.9969460
PFNA	4.362	0.0005 – 1	Y = 18021400X + 10132.21	0.9919629
PFOS	4.357	0.0005 – 1	Y = 9036007X + 4634.707	0.9959911
8:2FTS	4.737	0.0005 – 1	Y = 13503830X + 22019.94	0.9910791
PFDA	4.731	0.0005 – 1	Y = 20721320X + 6159.003	0.9988183
N–MeFOSAA	4.910	0.0005 – 1	Y = 5175350X – 4205.132	0.9967154
FOSA	4.788	0.0005 – 1	Y = 10845680X – 3958.125	0.9906969
PFDS	5.029	0.0005 – 1	Y = 16045680X + 2859.679	0.9960250
PFUdA	5.050	0.0005 – 1	Y = 15360260X + 6624.184	0.9980635
N–EtFOSAA	5.071	0.0005 – 1	Y = 7813284X + 2304.237	0.9966902
PFDoA	5.330	0.0005 – 1	Y = 10646190x – 687.5052	0.9933519
10:2FTS	5.353	0.0005 – 1	Y = 15338050X + 4246.053	0.9952768
N–MeFOSE–M	5.221	0.0005 – 0.1	Y = 2650452X + 6543.635	0.9650257
N–MeFOSA–M	5.224	0.01 – 1	Y = 20094250X – 257435.0	0.9841030
PFTrDA	5.572	0.0005 – 0.1	Y = 2557403X + 759.2317	0.9929004
N–EtFOSE–M	5.396	0.0005 – 0.1	Y = 4045844X + 14469.81	0.9822554
N–EtFOSA–M	5.407	0.0005 – 0.1	Y = 4082369X – 854.3064	0.9735044
PFTeDA	5.786	0.0005 – 0.1	Y = 23611250X + 5059.004	0.9951475

* Preliminary results

MRM transitions were optimized and a 8-point calibration curve, ranging from 0.0005 – 1 µg/L (ppb), was generated for each PFAS (Table 3). Preliminary studies on the method performance were conducted to give method detection limits of 0.1 ppt and calibration ranges of 0.5 – 1000 ng/L for most PFAS compounds. Good linearity, R^2 of more than 0.99 in the stated calibration range, were obtained for most of the PFAS compounds (Table 3).

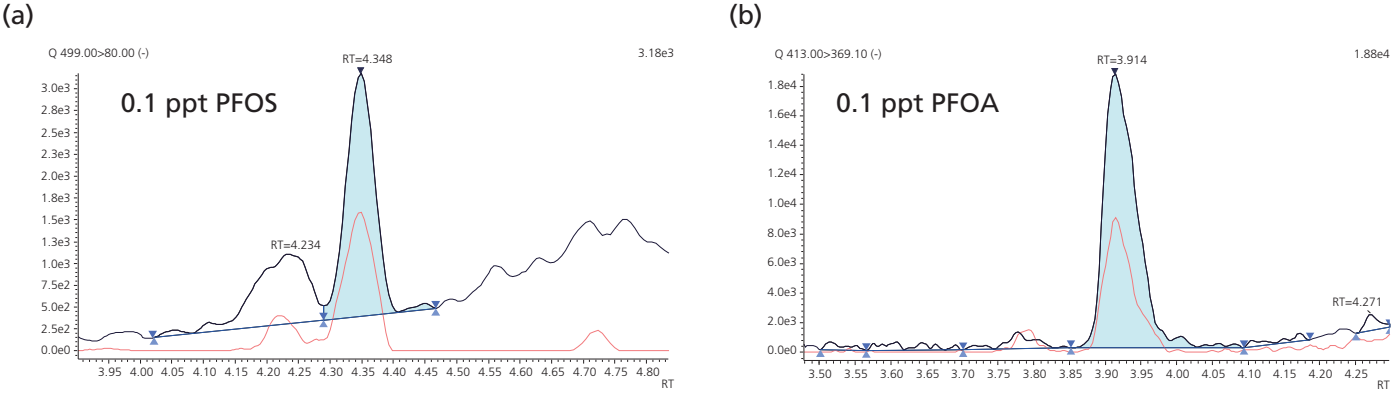

Figure 5. MRM Chromatograms of (a) PFOS and (b) PFOA at a concentration of 0.1 ppt

PFAS Analysis in Real Tap Water Samples

Real tap water samples were collected and analyzed using the described automated SPE and LC-MS/MS method. Predominantly, the two major PFAS compounds, PFOS and PFOA, were detected at low ppt range in the tap water samples (Figure 6).

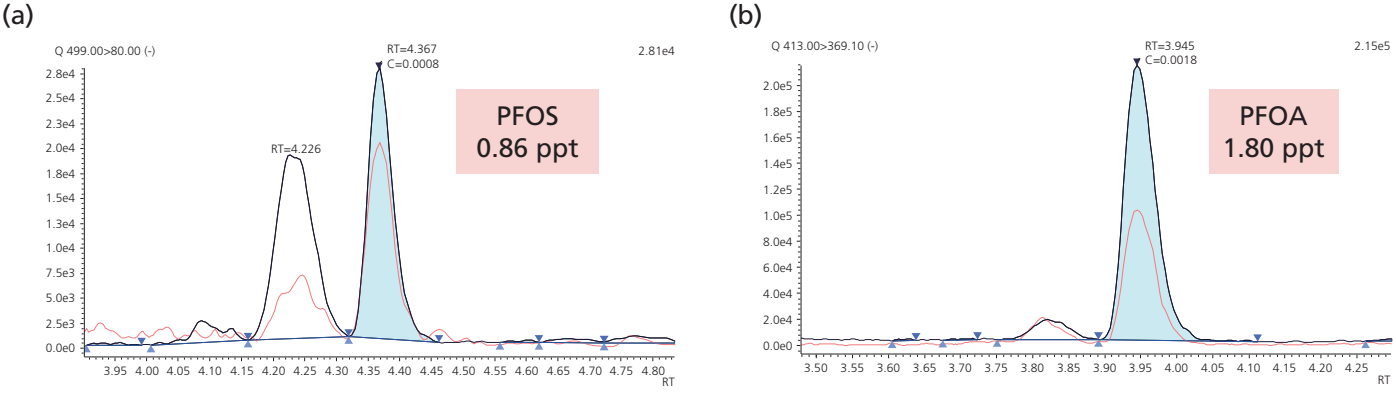

Figure 6. Mass chromatograms of (a) PFOS and (b) PFOA detected in real tap water samples

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Alternative Method for PFAS Analysis

Alternatively, an online trapping method where 2 mL of sample can be trapped and subsequently eluted onto an analytical column for quantitative analysis.

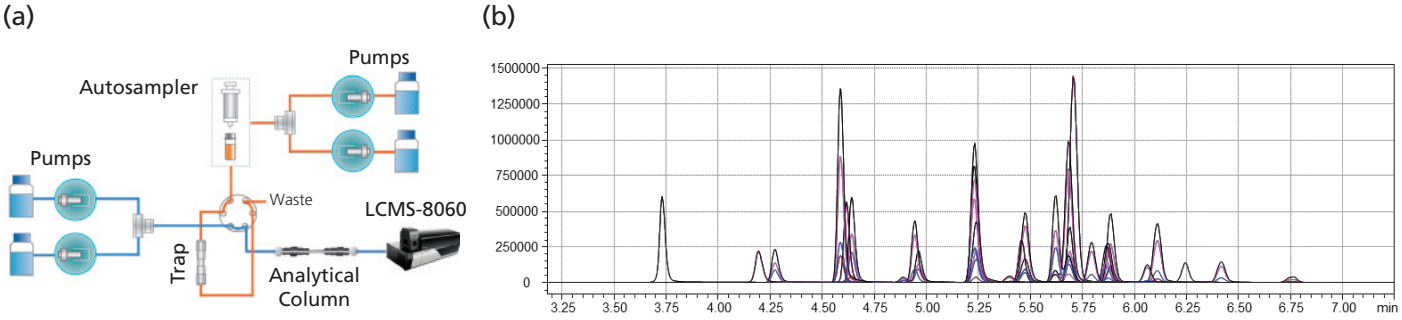

Figure 7. Online trapping PFAS method: (a) LCMS setup and (b) Preliminary chromatograms of PFAS

Conclusion

- Demonstrated an effortless sample preparation of environmental water samples
- Conducted an ultra-fast 7-min LC-MS/MS method for the quantitation of 62 PFAS
- Preliminary results showed trace-level (ppt) detection of PFAS compounds
- Future work on method validation (e.g. repeatability, recovery and precision) ongoing

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