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Analysis of Per/Polyfluoroalkyl Substances (PFASs) in Water using the Ultivo Triple Quadrupole LC/MS

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Introduction

Per/Polyfluoroalkyl substances (PFASs) are widely used in manufacture and industry because of their desirable properties. They find uses as surfactants, fire-retardants, non-stick cookware and other applications. Their unique properties also make them persistent and they have been detected almost ubiquitously in the environment.

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. Several US states also have public health guidelines for PFASs ranging from 20-400 ng/L in drinking water.

This study describes a method for the sensitive quantification of 17 PFASs including all 14 in the USEPAs method 537 in drinking water. The analysis is performed in a single run using the Ultivo Triple Quad LC/MS system.

Innovative technologies within Ultivo allow for reduction in its overall footprint, while conserving the comparable performance level of much larger MS systems. Ultivo's numerous innovations such as the VacShield, Cyclone Ion Guide, Vortex Collision Cell and Hyperbolic Quads, not only maximize quantitative performance in a small package, but also enhance instrument reliability and robustness in order to have greater uptime. Moreover, Ultivo reduces the need for user intervention for system maintenance, making the system operation and maintenance manageable for non-expert MS users.

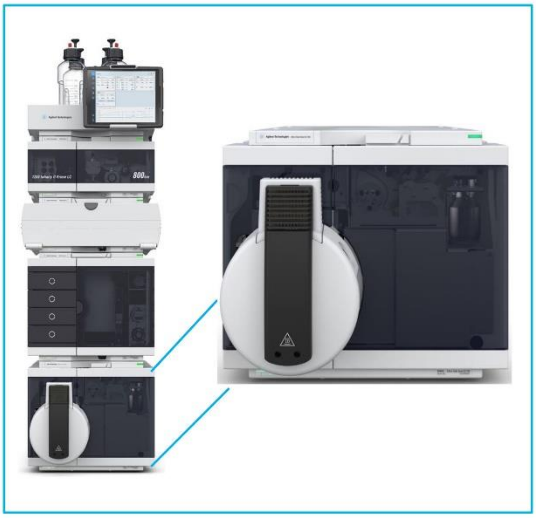

Figure 1. Ultivo Triple Quadrupole LC/MS

Experimental

Sample Preparation:

250 mL water samples were extracted using the Agilent SampliQ Weak Anion Exchange (WAX) cartridges.

Extraction conditions were similar to those in the EPA method 537 with a final extract in 96/4 (v/v) methanol (MeOH)/Water.

LC/MSMS Instrument Conditions:

Table 1. HPLC Parameters

1290 Infinity II LC Parameters	
Delay Column	Zorbax Eclipse Plus C18, 4.6x50 mm, 3.5 µm
Analytical Column	Zorbax Eclipse Plus C18, 3.0x50 mm, 1.8 µm
Injection Volume	5 µL
Column Temp.	50°C
Flowrate	0.4 mL/min
Mobile Phase	A: 5mM Ammonium Acetate in Water B: 5mM Ammonium Acetate in 95% MeOH
Runtime	19.0 min

Table 2. MRM transitions and Ret. Time for 17 PFASs

Compound	Precursor Ion	Product Ion	RT (min)
PFBA	213	168.9	3.88
PFPeA	263	218.9	6.52
PFBS	298.9	98.9 (80)	7.06
PFHxA	313	268.9 (119)	8.52
PFHpA	362.9	319 (169)	9.9
PFHxS	398.9	99 (80)	10.07
PFOA	413	369 (169)	11.05
PFNA	463	419 (169)	11.95
PFOS	498.9	99 (80)	11.95
PFDA	513	469 (218.7)	12.71
PFUdA	563	519 (218.7)	13.37
N-MeFOSAA	570	482.9 (418.9)	13.04
N-EtFOSAA	584	525.9 (418.9)	13.38
PFDS	598.9	99 (80)	13.32
PFDoA	613	569 (268.9)	13.93
PFTrDA	663	619 (169)	14.4
PFTeDA	713	669 (169)	14.82

Table 3. LC Gradient

Time (min)	% B
0.0	10
0.5	10
2.0	30
14.0	95
14.5	100

Table 4. Ultivo Triple Quad LC/MS conditions

MS Source Parameters	
Gas Temp.	230°C
Gas Flowrate	5 L/min
Sheath Temp.	350°C
Sheath Flowrate	12 L/min
Nebulizer	15 psi
Capillary	2500 V
Nozzle	0 V
Ionization	Negative ESI

Results and Discussion

Instrument Performance:

Excellent peak shapes and sensitive detection of all PFAS in water was achieved with the Ultivo.

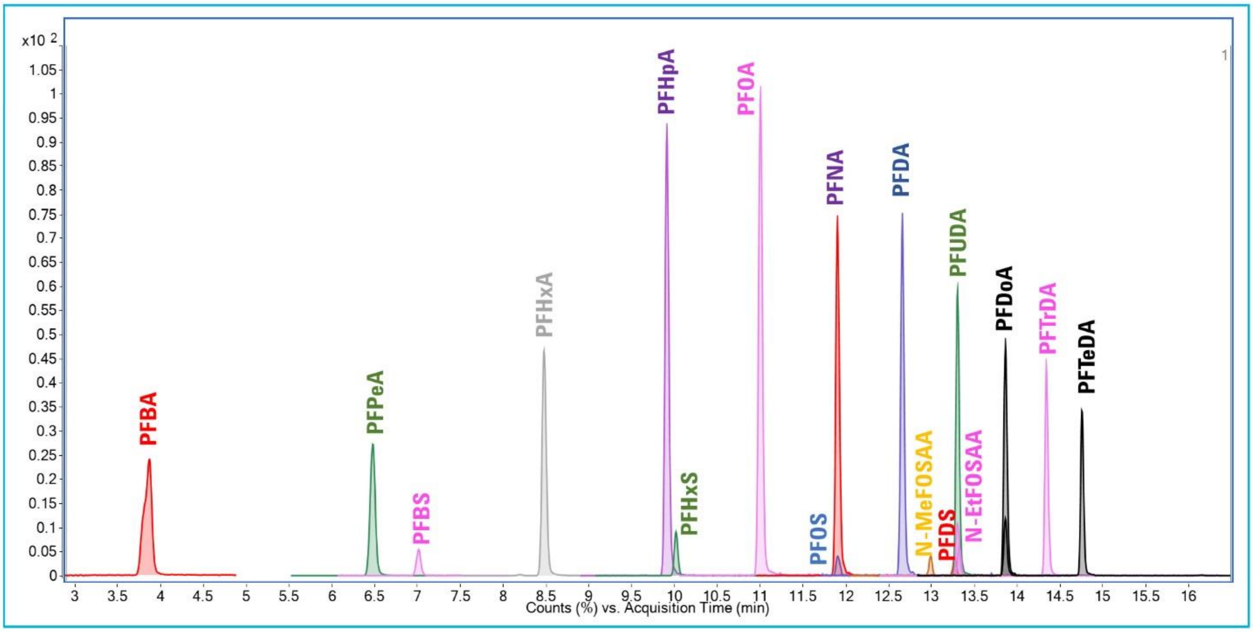

Figure 2. LC/MS/MS Chromatogram of the 17 Per/Polyfluoroalkyl substances (PFASs) analyzed at 1.0 ng/mL

Linearity and Sensitivity:

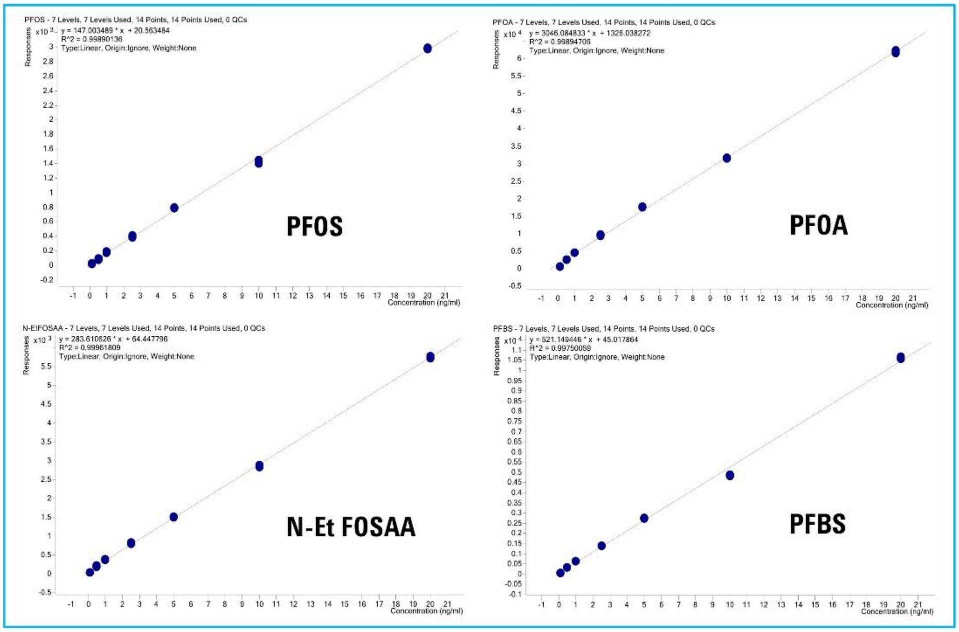

Figure 3. Calibration curves for PFOS, PFOA, N-Et FOSAA and PFBS.

All 17 PFASs ranging from 4-14 carbon-chain length had linear calibration curves with an **R^2 >0.99.**

Quantification using a seven point calibration curve at 0.1, 0.5, 1.0, 2.5, 5.0, 10 and 20 ng/mL were performed for all water samples.

Results and Discussion

Precision:

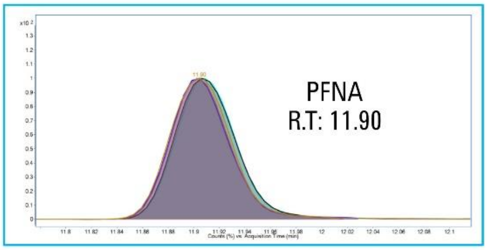

Figure 4. PFNA peak shape and retention time stability at 1 ng/mL with 5 replicate injections

Table 3. Precision expressed in RSD (%) for the 17 PFASs spiked at 1 µg/L (4 ng/L equil. In sample); n=5

Compound	RSD (%)	Compound	RSD (%)	Compound	RSD (%)
PFBA	0.28	PFOA	1.39	N-EtFOSAA	4.56
PFPeA	1.69	PFNA	0.98	PFDoA	2.43
PFBS	4.49	PFOS	5.30	PFTeDA	4.89
PFHxA	0.51	PFDA	1.62	PFTrDA	5.08
PFHpA	3.99	N-MeFOSAA	1.77	5 replicates spiked at 1 ng/mL	
PFHxS	4.72	PFUdA	2.93		

Recovery and RSD:

The recovery of the 17 PFASs were determined at 1 µg/L (4 ng/L equiv. in water) and 5 µg/L (20 ng/L equil. In water) shown in Figure 3. The overall recovery was between 70-125% for both spiking levels. Relative standard deviation was 0.3-10.8% for all compounds at both the 1 µg/L and 5 µg/L ng/mL spikes.

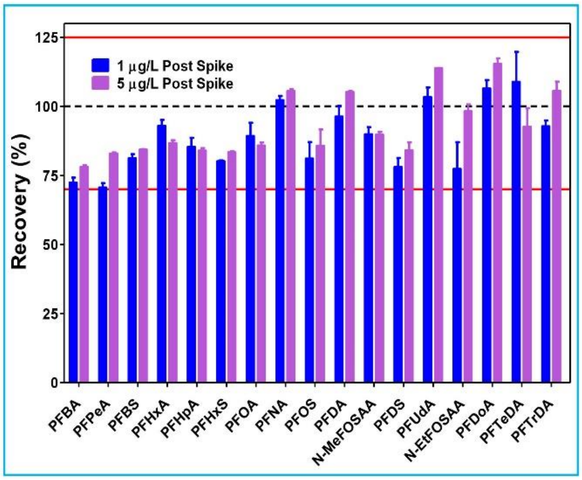

Figure 5. Recovery and RSDs for the PFASs evaluated at 1 and 5 ng/mL post-spiked into a water extract.

Analysis in Real Water Samples:

Finished drinking water samples from North-east USA and Canada were analyzed for the 17 PFASs using the extraction and analysis technique mentioned here. Figure 6 depicts the presence of PFOS and PFOA detected at low ng/L range in 2 samples along with the quantifier ion. The Ultivo was able to detect the presence of these low concentration PFASs suggesting good sensitivity and robustness for analysis of water samples.

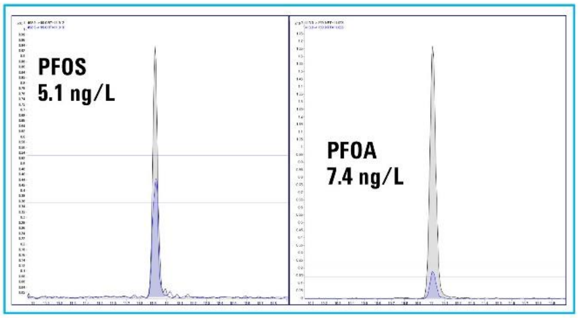

Figure 6. Overlay of qualifier and quantifier ion for PFOS and PFOA detected in finished drinking water samples at low ng/L levels using the Ultivo LC/MS/MS.

Conclusions

Ultivo Triple Quad LC/MS provides sensitive, reliable and robust quantification of PFAS in water.

- Excellent sensitivity for PFAS analysis with a reduced footprint
- Good recoveries and low RSDs achieved through innovative technologies
- Complete workflow & solution for PFAS analysis that includes the Infinity II LC, Ultivo Triple quad LC/MS and MassHunter software