ANALYSIS OF PER/POLYFLUOROALKYL SUBSTANCES (PFASs) IN WATER

Agilent Ultivo Triple Quadrupole LC/MS System

Figure 1. Agilent Ultivo Triple Quadrupole LC/MS integrated into the Agilent 1290 Infinity II LC.

Introduction

Per/Polyfluoroalkyl substances (PFASs) are widely used in manufacturing and industry due to their highly desirable properties. They are used as surfactants, fire-retardants, nonstick cookware coatings, and other applications. Because of their unique properties, 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 in drinking water, including all 14 in the USEPAs method 537. The analysis was performed in a single run using the Agilent Ultivo Triple Quadrupole LC/MS system.

Innovative technologies within Ultivo allow for reduction of its overall footprint, while conserving the comparable performance level of much larger MS systems. The numerous innovations of Ultivo not only maximize quantitative performance in a small package, but also enhance instrument reliability and robustness to provide greater uptime. Moreover, Ultivo reduces user intervention for system maintenance, making system operation and maintenance manageable for nonexpert MS users.

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Experimental

Sample preparation

Water samples (250 mL) were extracted using the Agilent SampliQ Weak Anion Exchange (WAX) cartridges. Extraction conditions were similar to those in EPA method 537 with a final extract in 96/4 (v/v) methanol (MeOH)/water.

LC/Triple quadrupole instrument conditions

Table 1. Agilent 1290 Infinity II LC parameters.

Parameter	Value
Delay column	Agilent ZORBAX Eclipse Plus C18, 4.6 × 50 mm, 3.5 µm
Analytical column	Agilent ZORBAX Eclipse Plus C18, 3.0 × 50 mm, 1.8 µm
Injection volume	5 µL
Column temperature	50 °C
Flow rate	0.4 mL/min
Mobile phase	A) 5 mM Ammonium acetate in water B) 5 mM Ammonium acetate in 95 % MeOH
Run time	19.0 minutes

Table 2. MRM transitions and RT for 17 PFASs.

Compound	Precursor ion	Product ion (secondary transition)	RT (min)
PFBA	213	168.9	3.88
PFPeA	263	218.9	6.52
PFBS	289.9	98.9 (80)	7.06
PFHxA	313	268.9 (119)	8.52
PFHpA	362.9	319 (169)	9.90
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)	14.40
PFTeDA	713	669 (169)	14.82

Table 3. LC Gradient conditions.

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

Table 4. Agilent Ultivo Triple Quadrupole LC/MS conditions.

Parameter	Value
Gas temperature	230 °C
Gas flow rate	5 L/min
Sheath temperature	350 °C
Sheath flow rate	12 L/min
Nebulizer	45 psi
Capillary	2,500 V
Nozzle	0 V
Ionization	Negative, ESI

Results and Discussion

Instrument performance

Excellent peak shapes and sensitive detection of all PFASs in water were achieved with the Ultivo LC/TQ.

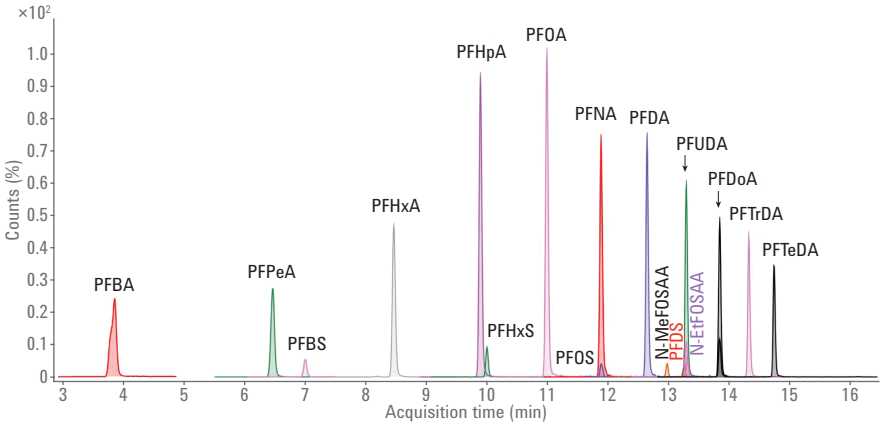

Figure 2. LC/Triple quadrupole chromatogram of 17 PFASs analyzed at 1.0 ng/mL.

Linearity and sensitivity

All 17 PFASs, with 4–14 carbon chain length, had linear calibration curves with 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 was performed for all water samples.

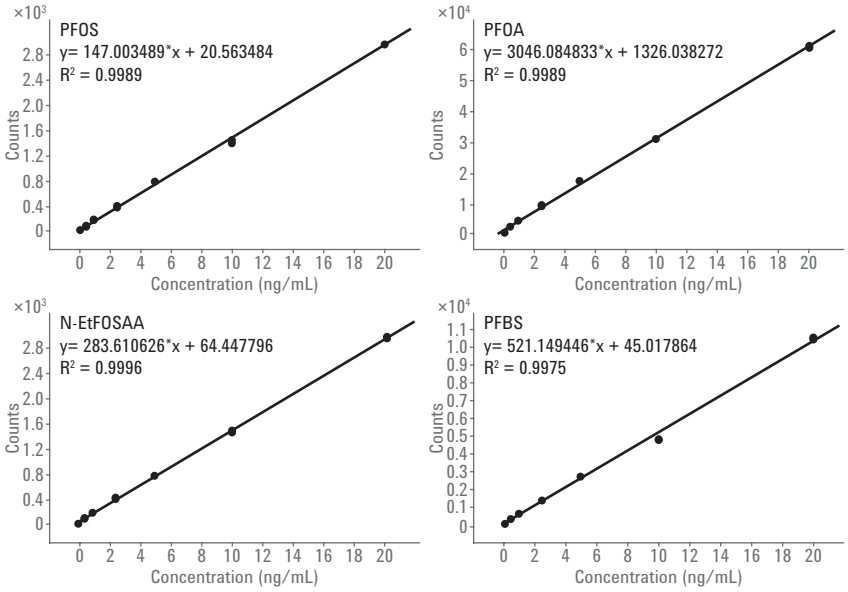

Figure 3. Calibration curves for PFOS, PFOA, N-Et FOSAA, and PFBS.

Precision

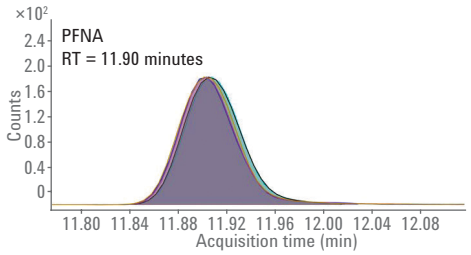

Figure 4. PFNA peak shape and retention time stability at 1 ng/mL with five replicate injections.

Table 5. Precision expressed in %RSD for the 17 PFASs post-spiked at 1 µg/L in a water extract (n = 5).

Compound	% RSD	Compound	% RSD
PFBA	0.28	**PFOS**	5.30
PFPeA	1.69	**PFDA**	1.62
PFBS	4.49	**N-MeFOSAA**	1.77
PFHxA	0.51	**PFUdA**	2.93
PFHpA	3.99	**N-EtFOSAA**	4.56
PFHxS	4.72	**PFDoA**	2.43
PFOA	1.39	**PFTeDA**	4.89
PFNA	0.98	**PFTrDA**	5.08

1 ug/L post spike is equivalent to 4 ng/L in the original water sample

Recovery and % RSD

Figure 5 shows the recovery of the 17 PFASs determined at 1 µg/L (4 ng/L equiv. in water) and 5 µg/L (20 ng/L equiv. in water) post-spiked into a drinking water extract. The overall recovery was between 70–125 % for both spiking levels. Relative standard deviation (RSD) was 0.3–10.8 % for all compounds at both the 1 µg/L and 5 µg/L spike levels.

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 Northeast USA 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 levels in two 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 the analysis of water samples.

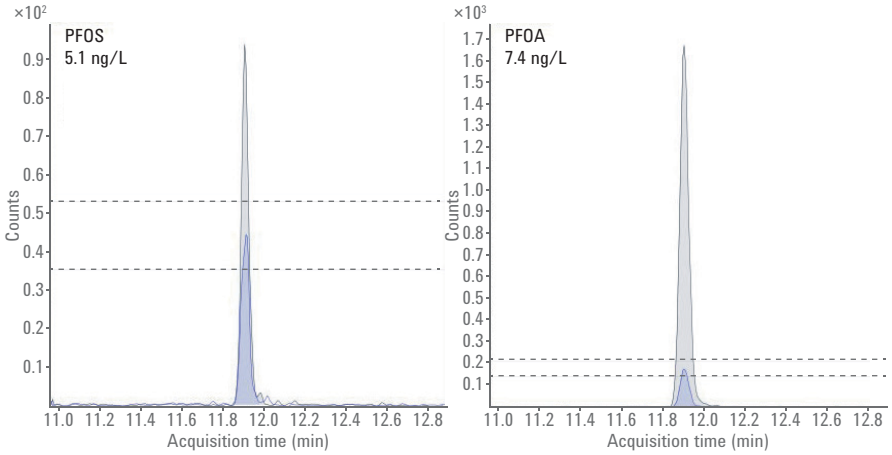

Figure 6. Overlay of qualifier and quantifier ion for PFOS and PFOA detected in finished drinking water samples at low ng/L levels using an Agilent Ultivo LC/TQ.

Conclusions

The Agilent Ultivo Triple Quadrupole LC/MS provides sensitive, reliable, and robust quantification of PFAS in water, including:

- Excellent sensitivity for PFAS analysis with a reduced footprint
- Good recoveries and low RSDs achieved through innovative technologies
- Complete workflow and solution for PFAS analysis that includes the Agilent 1290 Infinity II LC, Ultivo Triple Quadrupole LC/MS, and Agilent MassHunter software

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