

DETERMINATION OF LEGACY AND EMERGING PERFLUOROALKYL SUBSTANCES IN GROUND AND SURFACE WATERS USING LC-MS/MS WITH DIRECT INJECTION

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INTRODUCTION

Perfluoroalkyl substances (PFAS) are common persistent environmental contaminants used in the production of many consumer products as surfactants and for non-stick, stain, and water resistance coatings. PFAS are also a major component of fire fighting foams used for suppression of fuel fires. Global use of these compounds over decades has led to their release into the environment. Their chemical properties make them bioaccumulative and they are found throughout the environment, including in water, soil, sediment and biota. Current environmental quality standards, maximum limits and advisory guidelines, set in different parts of the world, require (sub) parts per trillion (ppt) detection of PFAS in various types of environmental samples.

An approach based upon ASTM 7979-17, using direct injection of water samples, was developed for the determination of a wide range of legacy and emerging (e.g. ADONA, F53-B) PFAS compounds. This approach has little sample preparation and requires a highly sensitive mass spectrometer for detection. Performance was assessed in surface, ground, and wastewater. By simplifying the sample preparation step, sample throughput can be drastically increased as well as reducing chances for sample contamination from inherent PFAS in typical laboratory supplies. The performance and scope of the expanded method makes it a suitable approach for the testing of water samples for a wide range of legacy and emerging, PFAS at relevant concentrations.

METHOD

Water Samples

- Water samples were provided by Dr. Lawrence Zintek from EPA Region 5. Samples included reagent, surface, ground, influent, and effluent wastewater, including water spiked with low and high concentrations of PFAS compounds from the ASTM 7979-17 method.
- 5 mL of sample was provided in a 15 mL Eppendorf tube.

Sample Pretreatment

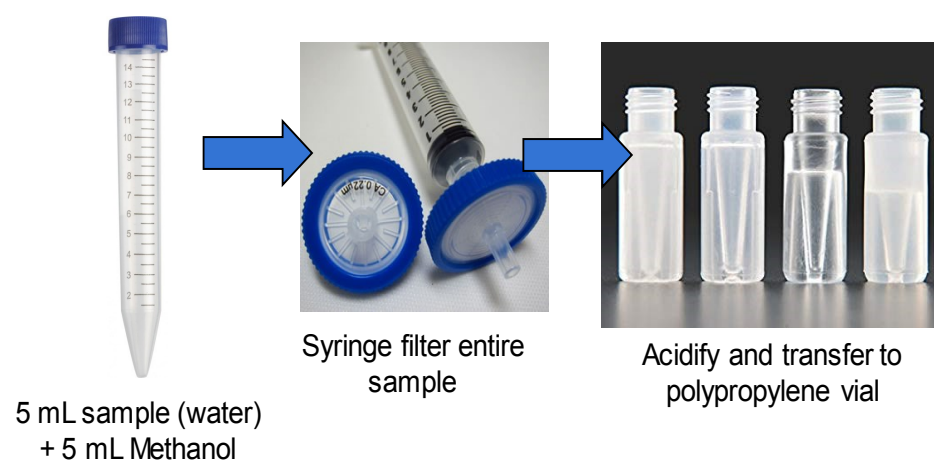


Figure 1. Overview of the sample pretreatment used

LC-MS/MS Conditions

LC System: ACQUITY UPLC I-Class Plus fitted with PFC kit
Column: ACQUITY CSH Phenyl Hexyl 2.1 x 100 mm, 1.7 µm
Column Temp: 35°C
Sample Temp: 10°C
Injection Volume: 30 µl

Mobile Phase A: 95:5 water:methanol + 2 mM ammonium acetate
Mobile Phase B: methanol + 2 mM ammonium acetate

Gradient:

Time (min)	Flow Rate (mL/min)	% A	% B
0	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
14	0.4	5	95
17	0.4	5	95
18	0.3	100	0
22	0.3	100	0

MS System: Xevo™ TQ-XS

Ionization Mode: ESI-

Capillary Voltage: 1.0 kV

Desolvation Temp: 500°C

Desolvation Gas Flow: 1100 L/hr

Cone Gas Flow: 150 L/hr

MRM parameters for each compound were optimised using the QuanOptimize tool in MassLynx.

RESULTS AND DISCUSSION

Method Detection Limits

A method detection limit (MDL) study was performed to assess the sensitivity of the sample analysis method using nine replicate samples of reagent water spiked with various concentrations of the PFAS analytes and 80 ng/L of the labelled standard solution. All samples were taken through the sample pre-treatment procedure prior to analysis. Table 1 highlights the MDL values for each compound which are well below the required reporting limits stated in the ASTM 7979-17 method. An MDL value could not be calculated for 6:2 FTS due to contamination of this compound in the solvents used for sample preparation.

Compound	Sample spike (ng/L)	MDL (ng/L)	Reporting range (ng/L)*	R ²
PFBA	100	25.20	50-2000	0.993
PFPeA	10	1.04	50-2000	0.999
PFHxA	10	1.33	10-400	0.999
PFHpA	10	0.91	10-400	0.999
PFOA	10	1.42	10-400	0.999
PFNA	10	1.32	10-400	0.999
PFDA	10	0.84	10-400	0.998
PFUnDA	10	2.52	10-400	0.996
PFDoDA	10	1.76	10-400	0.993
PFTriDA	10	2.34	10-400	0.991
PFTreDA	10	1.99	10-400	0.993
PFHxDA	200	25.41	-	0.984
PFOcDA	400	41.99	-	0.983
PFBS	10	1.21	10-400	0.999
PFPeS	10	1.07	10-400	0.999
PFHxS	10	1.41	10-400	0.999
PFHpS	10	1.57	10-400	0.999
PFOS	10	1.61	10-400	0.999
PFNS	10	1.67	10-400	0.999
PFDS	10	1.44	10-400	0.997
FOSA	10	1.29	10-400	0.999
N-Et-FOSAA	10	1.90	10-400	0.997
N-Me-FOSAA	10	1.59	10-400	0.999
N-Et-FOSA	10	1.45	-	0.997
N-Me-FOSA	10	1.19	-	0.999
FHUEA	10	1.53	10-400	0.999
FOUEA	10	1.36	-	0.999
8:2 diPAP	300	50.16	-	0.988
4:2 FTS	10	1.50	10-400	0.999
6:2 FTS	10	N/A	10-400	0.999
8:2 FTS	10	2.62	10-400	0.997
PFecHS	10	1.17	10-400	0.998
FHEA	200	42.19	300-8000	0.994
FOEA	200	50.38	200-8000	0.997
FDEA	200	79.48	200-8000	0.993
FHpPA	10	1.47	10-400	0.999
ADONA	10	0.82	-	0.999
9CI-PF3ONS	10	1.06	-	0.999
11CI-PF3OUdS	10	1.45	-	0.998

Table 1. Method Detection Limits (MDLs) for all PFAS in method. (*) the reporting ranges listed are specified in the ASTM 7979-17

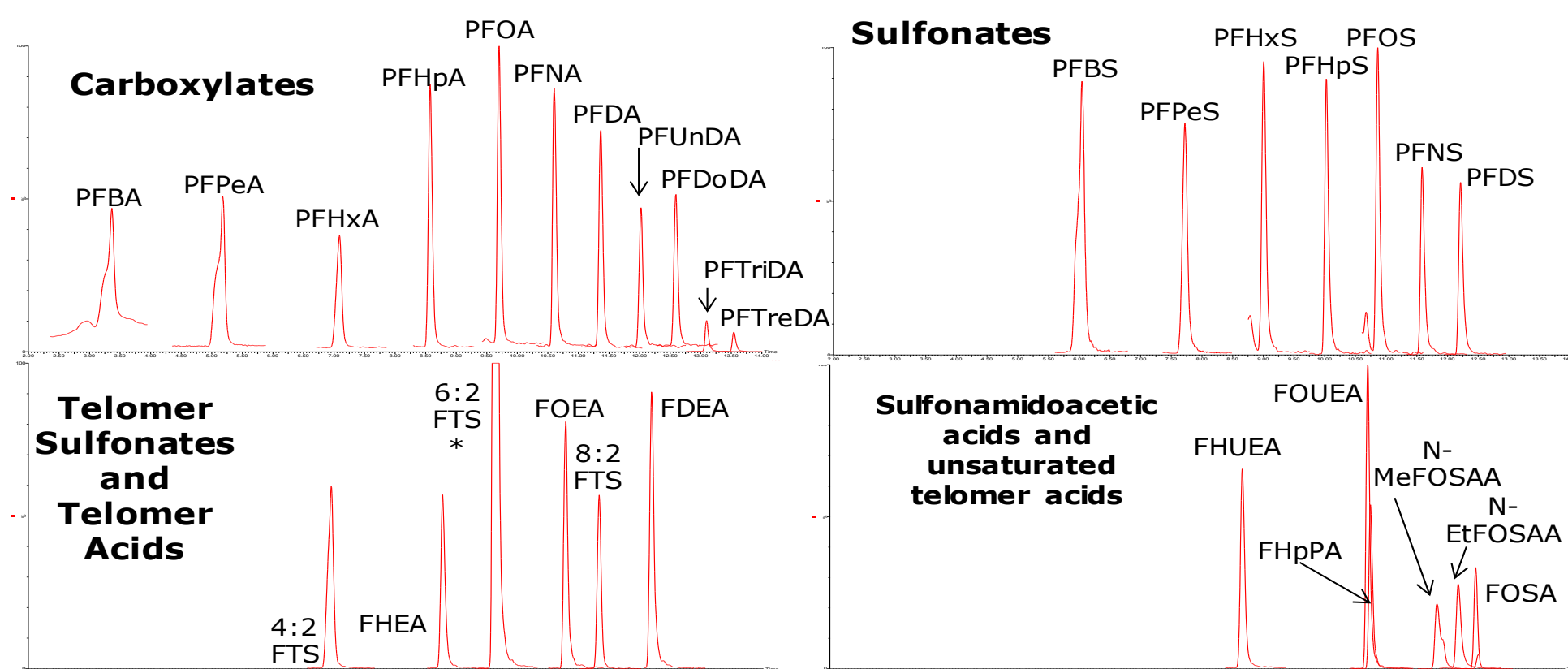


Figure 2. PFAS detected from the analysis of the low level spiked surface water sample; PFBA and PFPeA at 300 ng/L; 4:2, 6:2, and 8:2 FTS at 1200 ng/L; all other compounds at 60 ng/L

Trueness and repeatability

Trueness, determined using isotope labelled standards as surrogates, was typically in the range of 80-125%, with a few outliers due to matrix effects that could be mitigated by using matrix-matched calibration or standard addition. Repeatability was assessed by performing 20 replicate injections of a spiked surface water sample. Percent RSD of peak area for all PFAS over these 20 injections was < 10%.

Quality control

The ASTM 7979-17 method requires control samples to be run with the criteria they must pass as outlined in Figure 3. All compounds passed the control criteria, with the exception of 6:2 FTS due to contamination of solvent with that compound.

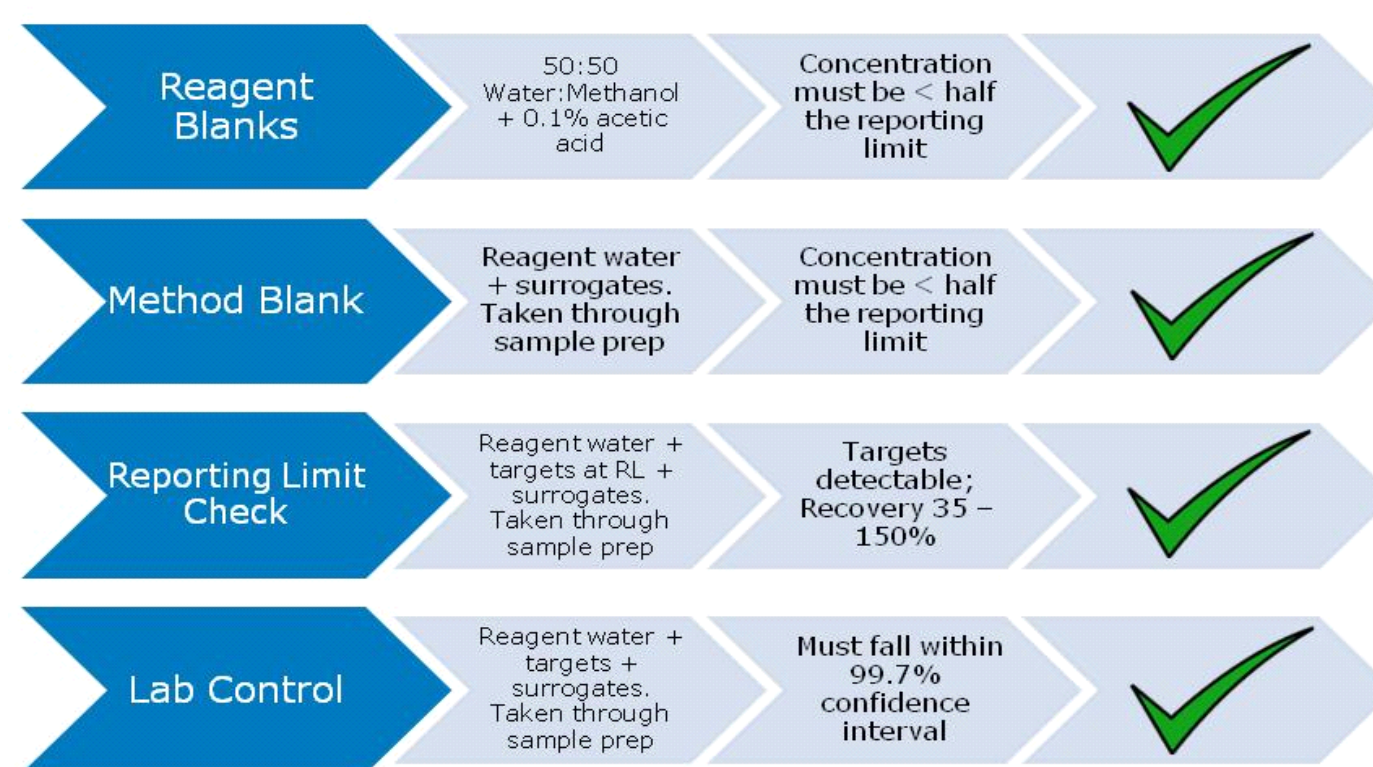


Figure 3. Criteria set by ASTM 7979-17 method for control samples

CONCLUSIONS

- The direct injection approach, based upon ASTM 7979-17, allows for quick sample turnaround time for the determination of a wide range of PFAS in water due to minimal sample preparation
- Results meet and exceed the ASTM 7979-17 method requirements
- Results show the method is suitable to check compliance with EPA health advisory acute levels of 70 ng/L PFOS
- The direct injection method used on the Xevo TQ-XS was extremely sensitive with method detection limits in the low ng/L range for many compounds, which could be improved upon by implanting large volume injection
- All PFAS compounds were detected in the spiked water samples with excellent trueness and repeatability
- For full details on this method, see Waters Application Note 720006329EN