

DETERMINATION OF LEGACY AND EMERGING PERFLUOROALKYL SUBSTANCES IN GROUND AND SURFACE WATERS USING LC-MS/MS FOLLOWING ENRICHMENT BY SPE

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INTRODUCTION

PFAS are common, persistent environmental contaminants used in the production of many consumer products. Due to their amphiphilic properties, they are used 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 widespread use of these compounds over decades has led to their release into the environment and PFAS are classified as persistent organic pollutants (POPs).

Currently, there are no legal regulations pertaining to PFAS monitoring in the USA, although the most common PFAS (PFOS and PFOA) are included in many advisory guidelines. The United States EPA has established a drinking water health advisory level of 70 ppt (ng/L) for total PFOS and PFOA. In Europe, the Water Framework Directive and Drinking Water Directive have set environmental quality standards and limits for PFAS, which range from the ppb to sub-ppt levels. As these limits are set at very low concentrations, there is clear need for highly sensitive analytical methods to detect PFAS in water samples.

One approach to reach sub-ppt levels is to perform enrichment prior to LC-MS/MS analysis. This poster describes the use of solid phase extraction (SPE) to enrich PFAS from water samples so that LC-MS/MS can be performed on the Xevo TQ-S micro. ISO 25101 was used as a starting point from which the scope of analysis could be expanded to a wider range of legacy and emerging PFAS, using weak anion exchange (WAX) for SPE. Forty legacy and emerging PFAS compounds, including GenX, were successfully incorporated into the final method. The performance of the method was assessed using four types of environmental water samples; surface water, ground water and wastewaters.

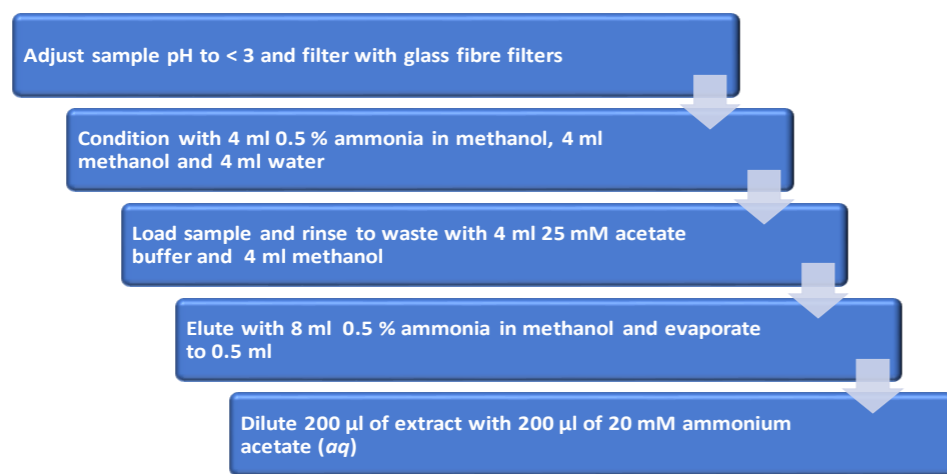
METHOD

Water Samples

- Surface and ground water samples were collected locally. Wastewater samples were provided by Dr. David Reckhow of University of Massachusetts Amherst.
- All samples were collected in 250 mL HDPE bottles and the entire sample was extracted.

Solid Phase Extraction Method

- The SPE method used for sample preparation was adapted from ISO 25101 using Oasis WAX, 6cc, 150 mg cartridges.
- Resulting in a 250x enrichment.



LC-MS/MS Conditions

LC System: ACQUITY UPLC I-Class Plus fitted with PFC kit
Column: ACQUITY UPLC BEH C18 2.1 x 100 mm, 1.7 µm
Column Temp: 35°C
Sample Temp: 10°C
Injection Volume: 10 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-S micro
Ionization Mode: ESI-
Capillary Voltage: 0.5 kV
Desolvation Temp: 350°C
Desolvation Gas Flow: 900 L/hr
Cone Gas Flow: 100 L/hr
Source Temperature: 100°C

MRM parameters for each compound were optimized using the QuanOptimize tool in Masslynx.

RESULTS AND DISCUSSION

Sensitivity and linearity

The method covers 40 native PFAS from a number of classes:

C4 - C18 carboxylates, C4-C10 sulfonates, telomer acids and sulfonates, various precursors, and emerging PFAS including GenX, ADONA, 9CI-PF3ONS, 11CI-PF3OUdS, NFHDA, PFEEESA, and PFMBBA.

It also includes 28 isotope labelled PFAS used as internal standards.

Compound	LOD vial (ng/L)	LOD sample (ng/L)	R ²
PFBA	10	0.04	0.999
PFPeA	10	0.04	0.999
PFHxA	10	0.04	0.999
PFHpA	5	0.02	0.999
PFOA	< 2	< 0.01	0.999
PFNA	10	0.04	0.999
PFDA	10	0.04	0.999
PFUnDA	10	0.04	0.999
PFDoDA	10	0.04	0.999
PFTriDA	10	0.04	0.993
PFTreDA	10	0.04	0.999
PFHxDA	500	2.00	0.994
PFoCDA	2000	8.00	0.988
PFBS	4.4	0.02	0.999
PFPeS	4.7	0.02	0.999
PFHxS	3.7	0.01	0.999
PFHpS	9.5	0.04	0.999
PFOS	3.65	0.01	0.999
PFNS	4.8	0.02	0.999
PFDS	9.6	0.04	0.999
N-EtFOSAA	10	0.04	0.999
N-MeFOSAA	5	0.02	0.999
FHUEA	5	0.02	0.999
FOUEA	5	0.02	0.999
8:2 diPAP	500	2.00	0.997
4:2 FTS	23.4	0.09	0.999
6:2 FTS*	< 95	< 0.38	0.999
8:2 FTS	9.6	0.04	1.000
PFecHS	9.2	0.04	0.999
FHEA	20	0.08	0.999
FOEA	8	0.03	0.999
FDEA	20	0.08	0.999
FHpPA	5	0.02	0.999
GenX	20	0.08	0.999
ADONA	< 2	< 0.01	0.999
9CI-PF3ONS	< 1.9	< 0.01	0.999
11CI-PF3OUdS	9.42	0.04	0.996
NFHDA	5	0.02	0.999
PFEEESA	< 2	< 0.01	0.999
PFMBBA	< 2	< 0.01	0.999

Table 1. Limits of detection and calibration correlation coefficients

Trueness

Figure 1 shows measured recoveries; absolute and adjusted (corrected by the use of isotope labelled internal standards) for PFAS, spiked into groundwater at 4-16 ng/L, depending upon the compound. Values for the majority of the PFAS compounds were within the range of 75 - 130% when using internal standards. PFBA and 6:2 FTS exhibited excessively high recoveries but this is likely to be due to background contamination in the laboratory.

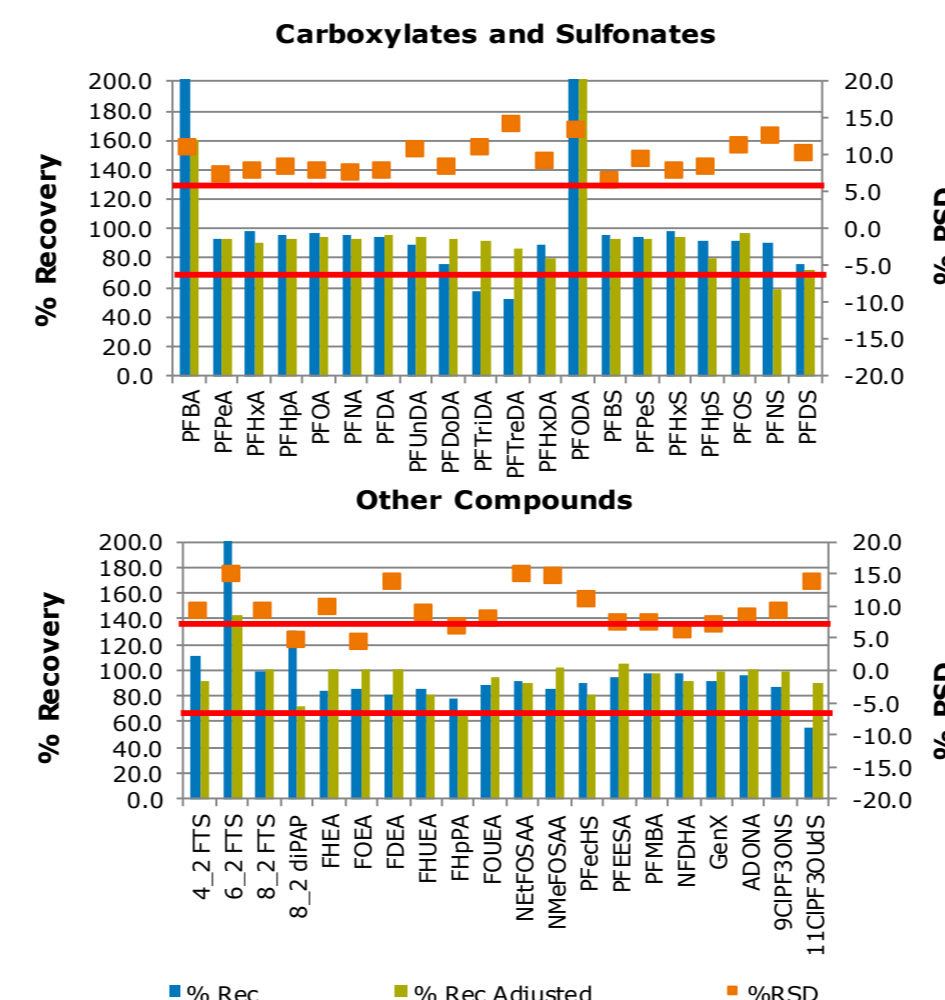


Figure 1. Recoveries and repeatability from six replicates of a ground water spiked at 4-16 ng/L, depending upon the compound

Repeatability

Repeatability of the method was assessed from the analysis of six replicates of the spiked ground water and %RSD shown in Figure 1. All PFAS exhibited % RSDs < 15%, with most < 10%.

Robustness

The robustness of the LC-MS/MS method was assessed by making twenty replicate injections of a spiked surface water extract (4-16 ng/L). The stability of peak areas, retention times and ion ratios are shown in Figure 2 for PFOA. Precision of measurements were good with %RSDs < 10% seen for all PFAS.

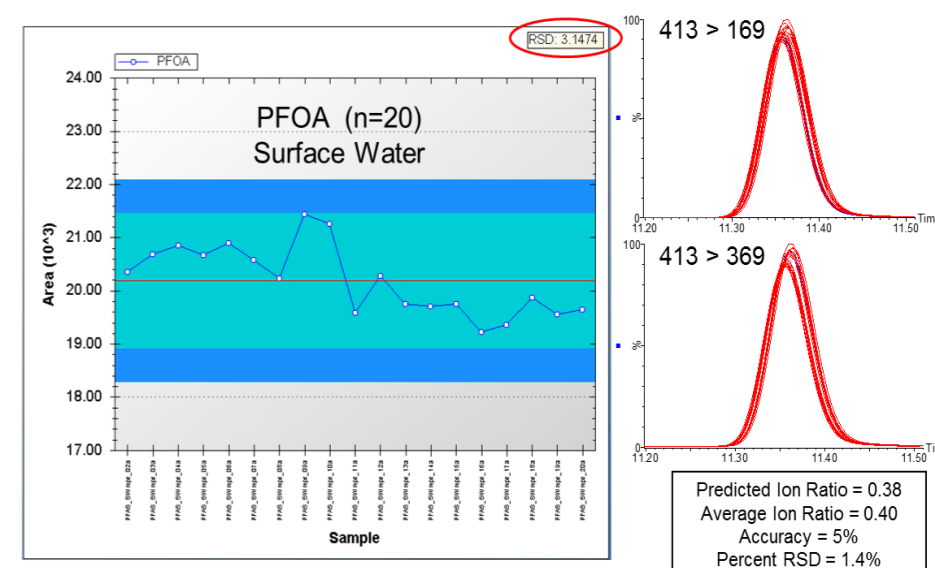


Figure 2. Peak areas for PFOA for each injection (RSD 3%) and overlay of peaks from replicate injections

Analysis of environmental water samples

Samples of four different types of water were analysed; surface, ground, influent wastewater and final effluent wastewater. A range of different PFAS were detected at varying concentrations in all samples. Figure 3 shows the distribution of PFAS in the water samples.

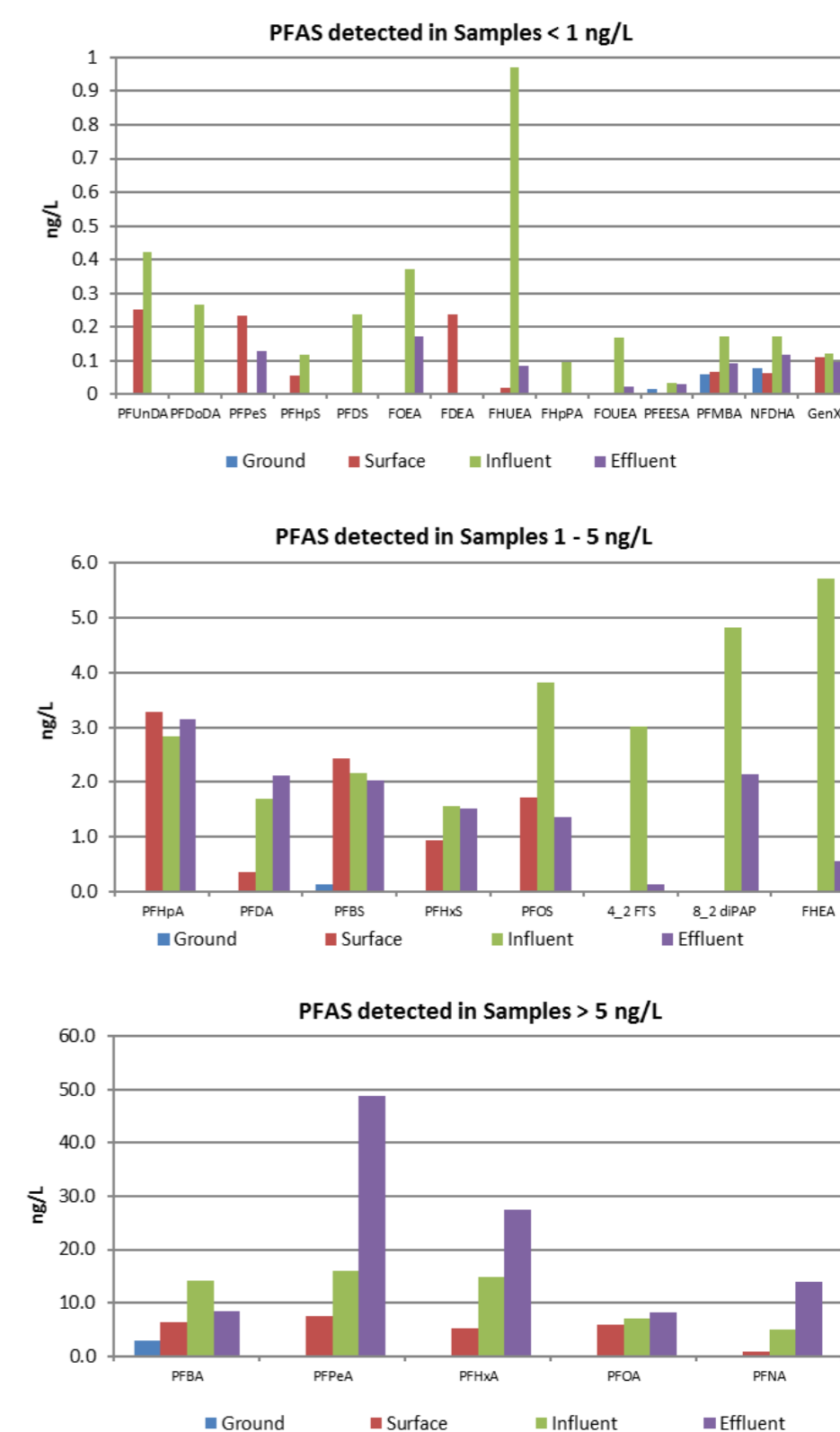


Figure 3. Distribution of PFAS in different water samples

CONCLUSIONS

- The method, based upon ISO 25101, has been used for the determination of both legacy and emerging PFAS
- SPE using Oasis WAX allows for extraction of a wide range of PFAS
- Using SPE provides a 250x enrichment from the water sample allowing for analysis using the Xevo TQ-S micro
- The method described is robust and has been applied to the analysis of a various range of environmental water samples including surface, ground and wastewaters
- Detection limits achieved with this method are sufficiently low for it to be used to check compliance with limits in European regulations and the EPA health advisories
- For full details on this method see Waters Application Note 720006471EN