DETERMINATION OF LEGACY AND EMERGING PERFLUOROALKYL SUBSTANCES (PFAS) IN WATER SAMPLES USING LC-MS/MS

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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 nonstick, 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, 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 levels of PFOS and PFOA. In Europe, the Water Framework Directive and Drinking Water Directive have set minimum quality standards of PFOS and PFOA which range from the ppb to sub-ppt levels. Such examples of monitoring guidelines demonstrate the need for highly sensitive analytical measurements to detect PFAS.

One approach to reach sub-ppt levels is to perform sample enrichment prior to LC-MS/MS analysis. Sample prep similar to that described in ISO 25101 method is typically applied for enrichment of PFAS in environmental water samples. ISO 25101 was used as a guide to expand the analysis to a wider range of legacy and emerging PFAS using weak anion exchange (WAX) for solid phase extraction (SPE) prior to analysis. 40 legacy and emerging PFAS compounds, including GenX, were successfully incorporated into the final method. The method was assessed using four types of environmental water samples (surface water, ground water, influent waste water and final effluent waste water).

METHODS

Water Samples

Surface and ground water samples were collected locally. Waste water samples were graciously 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 (Figure 1) was adapted from **ISO 25101.**
- SPE was performed using **Oasis WAX**, 6cc, 150 mg cartridges.
- The eluent was dried to a final volume of 0.5 mL, resulting in a **250x enrichment.**

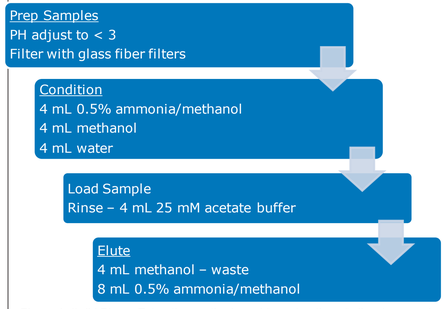

Figure 1. Solid Phase Extraction method used for extraction of all water samples.

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.

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For full details on this method, please see Waters Application Note 720006471EN

Limit of Detection (LOD) for each compound is shown in Table 1 as both an in vial concentration (after enrichment), and an in sample concentration (before enrichment).

Detection Limits

The method contained 40 native PFAS and 28 isotope labelled PFAS used as internal standards. The full list of compounds included can be found in Table 1. In summary, the method covered the following classes: C4 - C18 carboxylates, C4 - C10 sulfonates, telomer acids and sulfonates, various precursors, and emerging PFAS (GenX, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, NFHDA, PFEESA, PFMBA).

Limit of Detection (LOD) for each compound is shown in Table 1 as both an in vial concentration (after enrichment), and an in sample concentration (before enrichment).

Table 1. Limit of detection and linearity for PFAS tested in the method.

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
9Cl-PF3ONS	< 1.9	< 0.01	0.999
11Cl-PF3OUdS	9.42	0.04	0.996
NFHDA	5	0.02	0.999
PFEESA	< 2	< 0.01	0.999
PFMBA	< 2	< 0.01	0.999

RESULTS AND DISCUSSION

Method Performance

Performance of the sample preparation method is summarized in the recovery values highlighted in Figure 2 which shows recovery (blue bars) and adjusted recovery (green bars). Adjusted recovery values were calculated by using the isotope labeled internal standards to correct for loss through sample prep. A majority of the PFAS compounds fell within the recovery range of 75 - 130% when using the internal standards to calculate concentrations. PFBA and 6:2 FTS resulted in high recoveries, but they are known contaminant compounds in the laboratory.

Repeatability of the method was assessed from the analysis of six replicates of ground water spiked with the PFAS mix. The orange squares in Figure 2 represent the % RSD of the six replicates of ground water taken through the entire sample preparation method and analysis. All PFAS had a % RSD below 15%, with most being below 10%. This indicates the sample analysis method is reproducible.

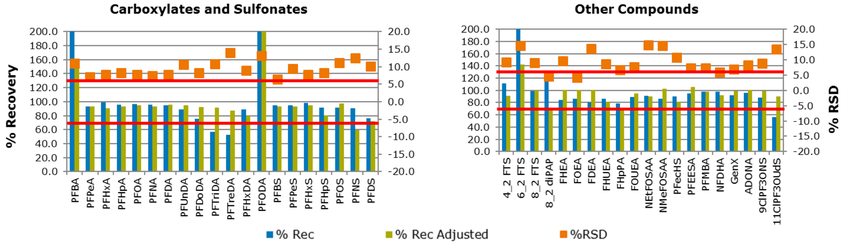

Figure 2. Method recovery (blue bars/left axis) and method reproducibility (orange squares/right axis) for all PFAS compounds covered in method. The adjusted recovery (green bars/left axis) represents the compound response corrected to its internal standard.

Method Robustness

The robustness of the instrument over a series of matrix injections was evaluated using a spiked surface water extract. Twenty replicate injections were performed to assess peak area, retention time, and ion ratio stability in a complex matrix. Stability of all three parameters over 20 injections are shown in Figure 3 for PFOA. Peak area is plotted to determine the %RSD, a peak overlay is shown to represent the retention time is not shifting, and ion ratio data indicates the ion ratios are stable. Overall, a %RSD of less than 10% was seen for all PFAS in the method.

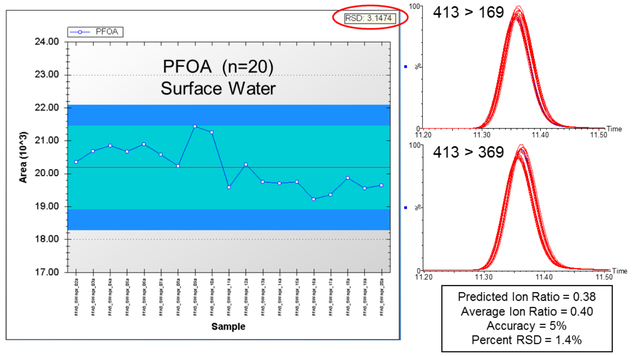

Figure 3. Repeatability assessed by 20 replicate injections of surface water. Peak area of PFOA for each injection is plotted in TrendPlot with an RSD of 3% (left) and the peak overlay of replicate injections with ion ratio information (right).

Analysis of Environmental Water Samples

Four different types of environmental water were extracted and analyzed to test the described method including surface, ground, influent, and final effluent water. A range of different PFAS were detected at varying concentrations in all samples. Figure 4 demonstrates the different patterns and concentrations of PFASs identified in the environmental water samples.

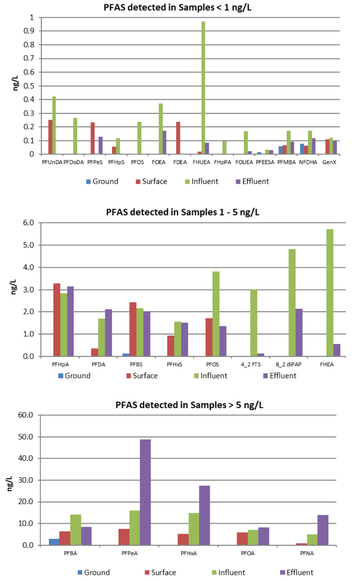

Figure 4. Patterns of PFASs detected in environmental water samples grouped by concentration level.

CONCLUSIONS

- **Using SPE preparation of water samples provides a 250x enrichment of the sample allowing for analysis using the Xevo TQ-S micro.**
- **Oasis WAX allows for successful extraction of a wide range of PFAS.**
- **Achievable detection limits with this method align with the necessary action levels set by the European Framework Directive and the EPA health advisory.**
- **Following the guidance of ISO 25101, analysis of environmental water samples can be accomplished for determination of both legacy and emerging PFAS.**
- **The method described is robust and has been applied to the analysis of a various range of environmental water samples including surface, ground, and waste waters.**