Adaptation of Large Panels of Per- and Polyfluoronated Alkyl Substances (PFAS) for Routine Analysis of Drinking and Environmental Waters by Direct Injection Using UHPLC-MS/MS

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INTRODUCTION

Per- and Polyfluoroalkyl Substances (PFAS), are extremely persistent in the environment and can cause serious health problems if you are exposed to them even at low levels. Their production and use have resulted in severe contamination of soil, water and food. To protect public health, advisory and regulatory limits continue to be created and updated. Consequently, routine PFAS analysis has become challenging as not only low detection limits are required, but extensive compound coverage is a prerequisite nowadays. This list of PFAS covers both the regulated set of 20 PFAS compounds in the updated European Union Drinking Water Directive 2020/2184, and the 47 PFAS required to be monitored by the Drinking Water Inspectorate (DWI).

This simple, direct injection method for PFAS analysis utilizes our highly sensitive mass spectrometer to reach necessary performance criteria. The enhanced negative ion sensitivity of the Xevo™ TQ Absolute Tandem Quadrupole Mass Spectrometer enables PFAS analysis with a reduced sample injection volume of 50 µL without compromise to method performance. Performance has been shown in a variety of water matrices covering drinking water and environmental water. Method detection limits of 48 compounds were determined to range from 0.1–3.1 ng/L.

METHOD PARAMETERS

Sample preparation and analysis:

Samples were prepared using the dilution protocol in Figure 1. Analysis was performed on ACQUITY™ Premier System FTN with PFAS Analysis Kit coupled to Xevo TQ Absolute Mass Spectrometer (figure 2.).

A calibration ranging from 0.5 to 200 ng/L was used for all analytes. Quantification of spiked samples were calculated using matrix matched bracketed calibration prepared in respective blank matrix extract.

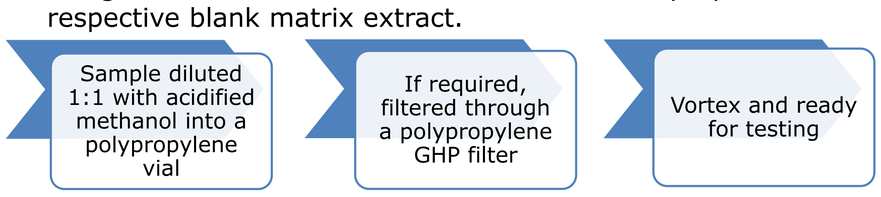

Figure 1. Sample preparation workflow

Challenges of overcoming background contamination: Deviation of the chromatographic system and solvents can be unavoidable. Therefore, steps should be taken to minimise these contributions. An easily installed PFAS kit replaces items such as the conventional PTFE coated solvent lines with PFAS-free PEEK components. Installation of the isolator column prior to the sample, delays residual background interferences originating in the mobile phase. This can be seen in figure 3, where the background PFBA from the mobile phase is fully resolved from the analytical peak from the injected sample.

Key optimisation factors:

A careful balance is required for maximum performance when analysing short and long chain PFAS simultaneously.

- To increase the sensitivity of longer chain, less water soluble PFAS, diluting to a higher final organic content saw significant increases in recovery. However, for some short chain PFAS like PFBA, the peak shape deteriorated. A compromise of 50:50 sample dilution with methanol was chosen as optimum sample composition.
- Desolvation temperature is another key parameter that can be optimised to obtain significant gains in sensitivity. Certain labile PFAS favor low desolvation temperatures, the result of this is a compromise that has to be made when determining the optimum temperature to suit all analytes.

Sensitivity and robustness:

The enhanced sensitivity of the Xevo TQ Absolute Mass Spectrometer is demonstrated in Figure 4, showing the chromatogram of PFOS spiked into drinking water. In this example, both the branched and linear isomers are detectable using a 50 µL injection at 0.73 ng/L, allowing for accurate quantitation of all isomers near detection limits.

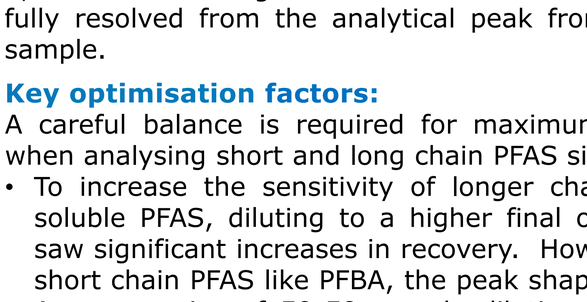

Figure 4. PFOS spiked at 0.73 ng/L in soft drinking water, showing both branched and linear forms

- Method detection values obtained were typically <1 ng/L and under 4 ng/L for all 48 PFAS, full details are in table 1.
- Linearity was calculated using calibrations with a minimum of 6 levels, ranging from 0.5 ng/l to 200 ng/L dependent on compound
- All compounds achieved linear regression using 1/X weighting with R^2 values ≥0.990, with the only exceptions hard drinking water and mineral water where PFHxDA and PFTrDS had quadratic calibrations.

Instrumental conditions:

UHPLC System:	ACQUITY™ Premier System, fitted with Waters PFAS kit (p/n 205000588) and isolator column p/n (186009407)
Column:	ACQUITY UPLC ™ CSH ™ C18, 1.7 µm; 2.1 x 100 mm Column (p/n 186009461)
Mobile Phase A:	2 mM ammonium acetate in H2O:MeOH 95:5 (v/v)
Mobile Phase B:	2 mM ammonium acetate in MeOH
Column Temp:	40°C
Injection Vol:	**50 µL**

MS System:	Xevo TQ Absolute MS
Ionisation Mode:	UniSpray ™
Acquisition:	MRM
Capillary Voltage:	0.9 kV
Cone Gas Flow:	150 L/hr
Desolvation Temp:	400°C
Desolvation Gas Flow:	900 L/hr
Source Temp:	110°C

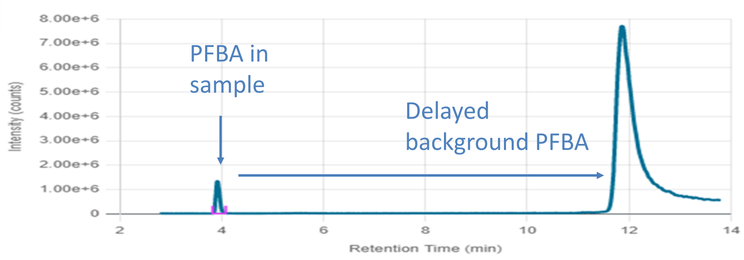

Figure 3. PFBA interference delayed from sample PFBA by the isolator column – Atlantis™ Premier BEH™ C18 AX Column

Care must be taken during the entire sample preparation to minimise any additional PFAS background. PFAS can be found in a consumables such as vials, caps and pipette tips. Methanol can also be a major source of PFAS contamination. It is essential to opt for a high-grade methanol for sample dilutions and monitoring batches regularly is recommended.

Figure 2. ACQUITY Premier LC System coupled with Xevo TQ Absolute MS

RESULTS AND DISCUSSION

Compound	MDL (ng/L)	Compound	MDL (ng/L)
11Cl-PF3OUdS	0.1	PFDoDA	0.2
3:3 FTCA	0.1	PFDoDS	0.2
4:2 FTS	0.1	PFDS	0.1
5:3 FTCA	0.1	PFecHS	0.4
6:2 FTS	0.3	PFEESA	0.1
7:3 FTCA	0.2	PFHpA	0.1
8:2 FTS	0.5	PFHpS	0.2
9Cl-PF3ONS	0.4	PFHxA	0.1
ADONA	0.1	PFHxDA	0.4
FBSA	0.1	PFHxS	0.1
FHxSA	0.2	PFMBA	0.1
FOSA	0.2	PFMOPrA	0.4
GEN-X	0.2	PFNA	0.2
HFPO-TA	0.7	PFNS	0.3
N-EtFOSA	0.1	**PFOA**	**0.1**
N-EtFOSAA	0.2	PFODA	0.1
N-EtFOSE	0.3	**PFOS**	**0.3**
N-MeFOSA	0.1	PFPeA	0.1
N-MeFOSAA	0.2	PFPeS	0.1
N-MeFOSE	0.2	PFTeDA	0.5
NFDHA	0.2	PFTrDA	0.3
PFBA	0.1	PFTrDS	0.4
PFBS	0.1	PFUnDA	0.2
PFDA	0.2	PFUnDS	0.1

Table 1. Method detection limits (MDL) calculated by analysing a set of 20 replicate 10 ng/L samples prepared in reagent water.

Linearity across different water types is shown in figure 5, where calibration data for soft and hard water, mineral water and river water all collected on one chart for PFNS and GenX. Both compounds obtained R^2 values of 0.999, for calibrations including all 4 water types. Where background PFAS in the sample was not an issue, matrix calibrations demonstrated recovery consistency across different water types allowing calibration using a common water source.

Recovery and repeatability across different water types are highlighted in figure 6. It shows 6 replicates in soft and hard water, mineral and river water each spiked at 10ng/L. The standard deviations of all 24 samples across the water types for both PFOA and PFTrDA were <20%.

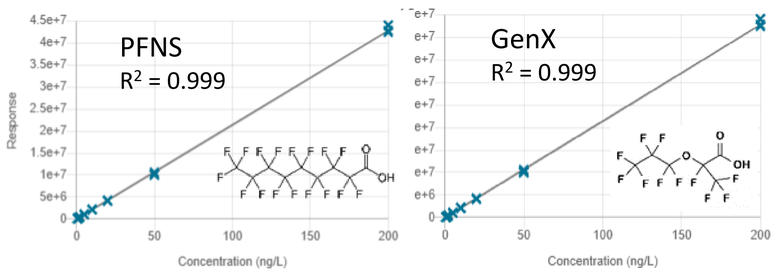

Figure 5. *Calibration data of two PFAS in soft and hard water, mineral water and river water demonstrating calibration curve linearity and calibration deviation %RSD over a range of different water types*

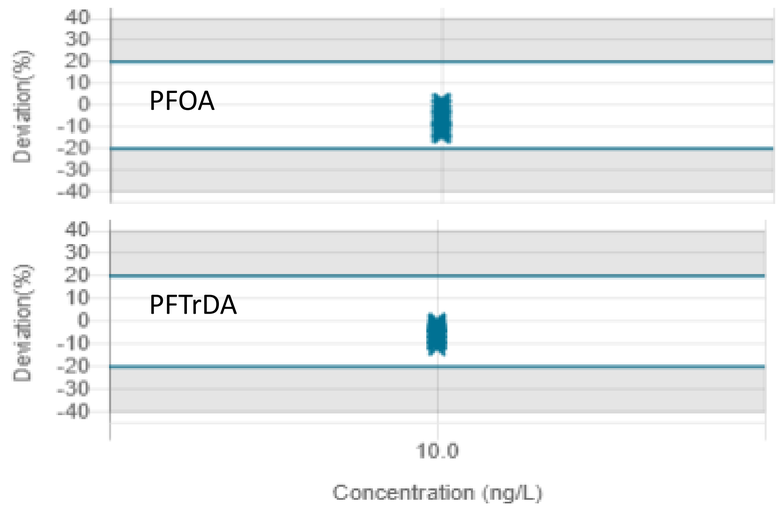

Figure 6. *Replicate data of 6 samples spiked at 10 ng/L in each soft and hard water, mineral water and river water, showing excellent reproducibility and recovery across different water types*

CONCLUSIONS

- Increased sensitivity to quantify PFAS in drinking and environmental water samples using a direct injection approach is achievable with analysis on the Xevo TQ Absolute MS.
- Minimal and rapid sample preparation using a dilute and shoot approach to increase laboratory throughput, while also reducing potential sources of sample contamination
- Reduced sample injection volume enables prolonged column lifetime, source cleanliness and increased system uptime, while ensuring suitable chromatography
- Method detection limits of 48 compounds were determined to be in the range of 0.1–3.1 ng/L

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