ULTIMATE SENSITIVITY FOR THE DETECTION OF PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN ENVIRONMENTAL WATER SAMPLES

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INTRODUCTION

Analysis of per- and polyfluorinated alkyl substances (PFAS) is now an essential part of water testing programs and is becoming a regular requirement for monitoring in environment and food sources. As regulations continue to be created and updated, the required method sensitivity has increased. Solid phase extraction (SPE) is one tool that can be utilized to enhance sensitivity of a method by enriching the sample prior to injection. The alternative is to use a direct injection method that relies on the sensitivity performance of the mass spectrometer. Direct injection has been gaining favorability as an option for PFAS analysis as it is a fast and simple preparation method, providing labs with the option of higher throughput of samples. Additionally, the samples are not subjected to as many solvents and lab consumables during their preparation, significantly reducing the potential for sample contamination and reduces solvent waste.

With the enhanced negative ion sensitivity of the Xevo™ TQ Absolute Tandem Quadrupole mass spectrometer, the boundaries of what is possible for the direct injection of PFAS in environmental samples have been expanded. Previous direct injection methods for the analysis of PFAS in water samples required relatively large volume injections of 30 and 50 µL to reach desired detection limits.[1,2] Using the Xevo TQ Absolute Mass Spectrometer, similar performance is achievable using only a 10 µL injection. Reducing the injection volume decreases the sample loading, allowing for better chromatographic performance, longer column lifetime, and less frequent intervention for source maintenance. These benefits help further enhance the ease and simplicity of the direct injection method for PFAS analysis.

METHODS

Water Samples
Drinking water, Ground water, and Surface Water samples were collected locally. Influent Wastewater was kindly provided by University of Massachusetts Amherst. All samples were collected in 5 mL portions.

PFAS Targeted
33 PFAS compounds were targeted in the MS/MS method including 11 carboxylates (C4-C14), 10 sulfonates (C4-13), 8 precursors (NMeFOSE, NEtFOSE, 4:2 FTS, 6:2 FTS, 8:2 FTS, FBSA, FHxSA, FOSA, NMeFOSAA, NEtFOSAA) and 4 emerging ethers (GenX, ADONA, 9ClPF3ONS, 11ClPF3OUdS).

Sample Prep
Samples were prepared according to the ASTM 7979 method.[3] 5 mL of each water sample was spiked with isotopically labelled extraction standards to measure recovery. Each sample was diluted with 5 mL methanol, vortexed, and then syringe filtered using a 1.0 µm glass fiber filter (prerinsed with acetonitrile and methanol). 10 µL acetic acid was added to each sample, as well as spiked with an isotopically labelled injection standard.

LC-MS/MS Conditions
LC System: ACQUITY™ UPLC™ I-Class Plus System fitted with PFAS Kit

Column: ACQUITY BEH™ C18 2.1 x 100 mm, 1.7 µm Column

Column Temp: 45°C

Sample Temp: 10°C

Injection Volume: 10 µl

Mobile Phase A: Water + 2 mM ammonium acetate

Mobile Phase B: Methanol + 2 mM ammonium acetate

Gradient:

Time (min)	Flow rate (mL/min)	%A	%B	Curve
0	0.35	95	5	initial
1	0.35	95	5	6
2	0.35	50	50	6
15	0.35	15	85	8
19	0.50	0	100	1
20	0.35	95	5	1
25	0.35	95	5	1

MS System: Xevo TQ Absolute Mass Spectrometer

Ionization Mode: ESI-

Capillary Voltage: 0.5 kV

Desolvation Temp: 350°C

Desolvation Gas Flow: 900 L/hr

Cone Gas Flow: 150 L/hr

Source Temperature: 100°C

RESULTS AND DISCUSSION

A Method Detection Limit (MDL) study was performed with results listed in **Table 1**. It is worth noting that the MDL values for PFBA, PFPeA, and 6:2 FTS are artificially high due to background contamination of these particular PFAS in the solvents used. Otherwise, MDLs for the 10 µL direct injection of water ranged from 0.8 – 2.0 ng/L, represented as the sample concentration prior to dilution.

Solvent calibration curves for selected compounds in the range of 0.5 – 250 ng/L can be seen in **Figure 1**. Data processing using the MS Quan application in waters_connect™ platform for quantitative analysis allows for easy visual representation and review of data quality.
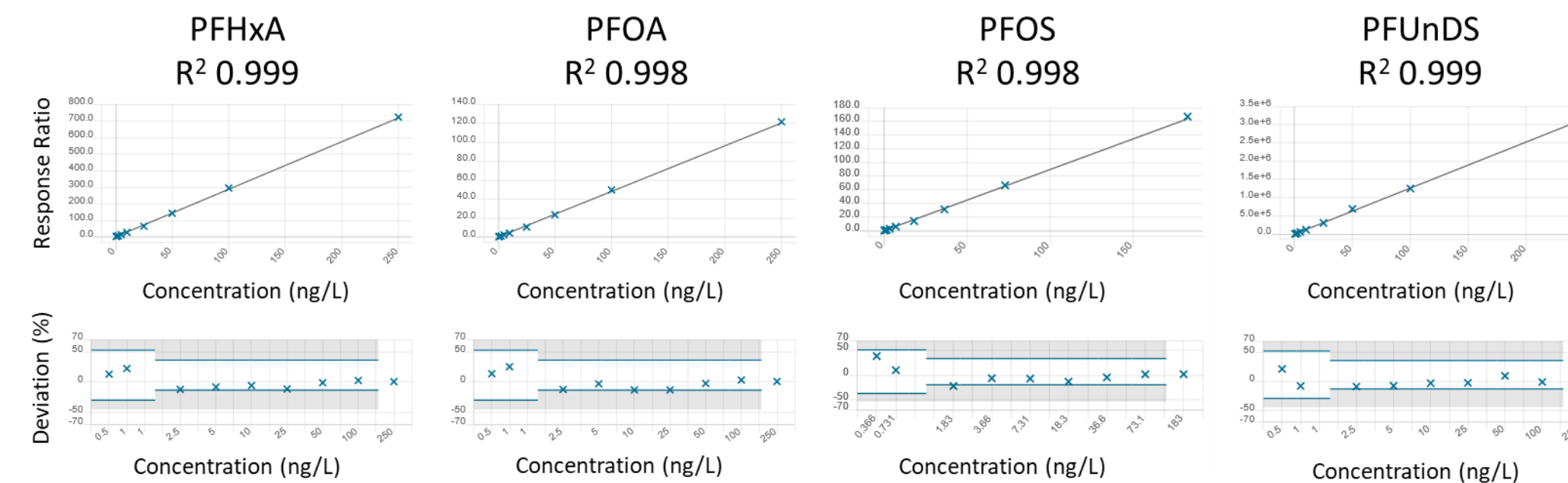

Figure 1. Calibration data of four PFAS compounds demonstrating calibration curve linearity and calibration deviation.

A variety of water samples ranging in complexity were evaluated using this method on the Xevo TQ Absolute Mass Spectrometer including drinking water, ground water, surface water, and wastewater. The sensitivity of the instrument is demonstrated in **Figure 2**, showing chromatograms of five different levels of PFOS spiked into the wastewater sample. In this example, both the branched and linear isomers are detectable at the lowest spike level, allowing for accurate quantitation of all isomers in the sample even near the detection limits. The concentrations of the PFAS detected in the four water samples are listed in Table 2. While two compounds were detected at higher concentrations in wastewater, the remaining PFAS quantified were all confidently detected below 5.0 ng/L using a 10 µL injection on the Xevo TQ Absolute Mass Spectrometer.
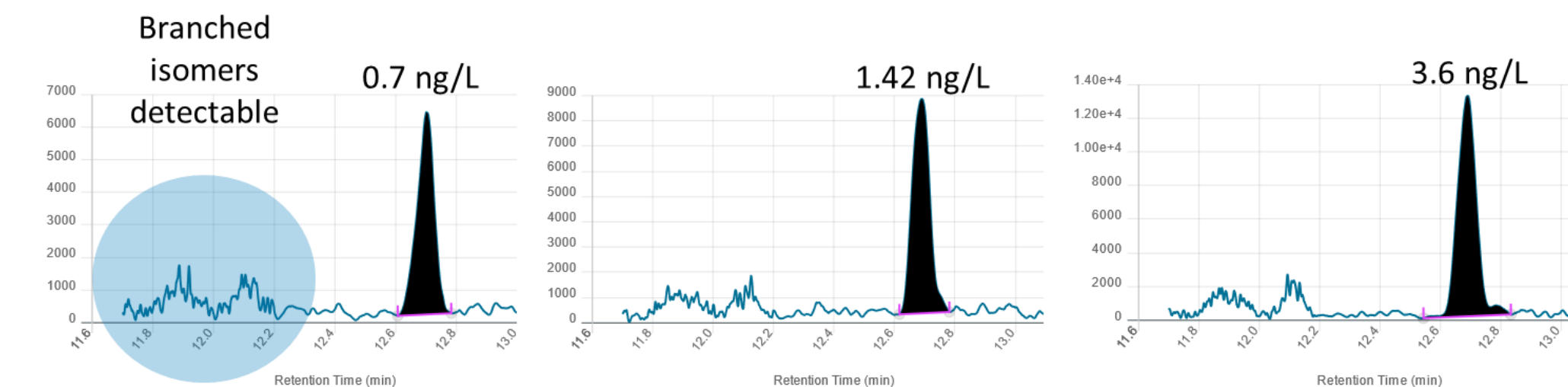

Figure 2. PFOS spiked into wastewater influent at various spiked concentrations (in-sample concentration reported).

Additionally, **Figure 3** demonstrates the stability of the method performance in the 10 ng/L continuing calibration verification (CCV) sample that was injected 7 times throughout the sample batch of approximately 120 samples. The precision of the calculated concentrations was within 10% RSD for all compounds in the method, with many below 5%.
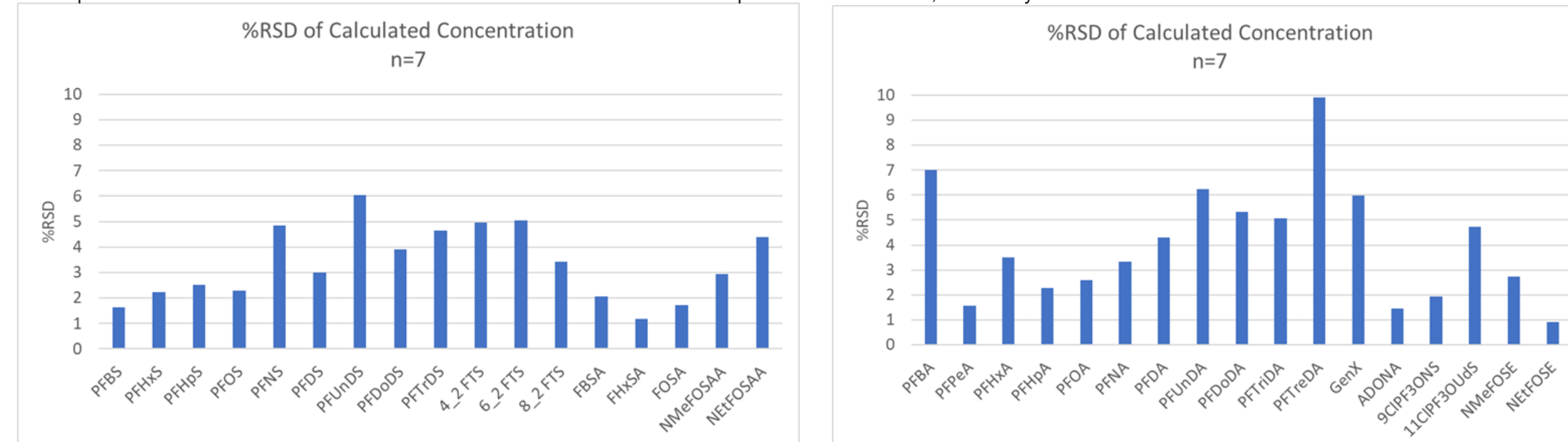

Figure 3. Precision (%RSD) of for calculated concentrations of n=7 injections of 10 ng/L CCV throughout a sample batch of over 120 injections.

Compound	Method detection limit (ng/L)	Compound	Method detection limit (ng/L)
PFBA	21.9	PFNS	1.3
PFPeA	7.7	PFDS	1.1
PFHxA	1.6	PFUnDS	1.7
PFHpA	0.8	PFDoDS	1.0
PFOA	1.2	PFTrDS	1.5
PFNA	1.2	GenX	1.1
PFDA	1.5	ADONA	0.9
PFUnDA	2.0	9Cl-PF3ONS	1.0
PFDoDA	1.5	11Cl-PF3OUdS	1.5
PFTriDA	1.4	4:2 FTS	1.4
PFTreDA	1.2	6:2 FTS	7.5
PFBS	0.8	FBSA	1.1
PFPeS	0.9	FHxSA	1.1
PFHxS	0.8	FOSA	1.1
PFHpS	1.0	N-Me-FOSAA	1.2
PFOS	1.0	N-Et-FOSAA	1.6

Table 1. Method detection limits (MDL) determined in reagent water prepared using the direct injection method using n=10 replicates.

	Concentration (ng/L)			
	Wastewater	Drinking water	Ground water	Surface water
PFHxA	17.4	4.6	3.8	3.8
PFHpA	4.1	2.0	2.0	2.2
PFOA	16.2	4.4	2.8	4.3
PFNA	2.5	<LLOQ	–	–
PFDA	1.6	–	–	–
PFBS	2.6	1.9	1.5	<LLOQ
PFHxS	1.2	<LLOQ	–	<LLOQ
PFOS	1.8	–	–	1.0
FBSA	<LLOQ	<LLOQ	–	<LLOQ
FOSA	<LLOQ	–	–	–
NMeFOSAA	2.7	–	–	–

Table 2. Concentrations of PFAS detected in water samples tested on the Xevo TQ Absolute Mass Spectrometer. <LLOQ signifies a positive identification, but concentration was not reported as it was below the calibration range.

CONCLUSION

- The enhanced negative ion sensitivity of the Xevo TQ Absolute Tandem Quadrupole Mass Spectrometer has allowed for utilization of the direct injection method for PFAS analysis without the need for a large volume injection, while maintaining method performance.
- The direct injection method for PFAS analysis was demonstrate using the Xevo TQ Absolute Mass Spectrometer in drinking water, ground water, surface water, and influent wastewater.
- Method detection limits of 33 compounds were determined to be in the range of 0.8 – 2.0 ng/L.
- PFAS were detected in water samples as low as 1.2 ng/L.
- The combination of the enhanced sensitivity of the Xevo TQ Absolute Mass Spectrometer, direct injection analysis and reduced injection volume allow a fast, accurate, high throughput option for PFAS sample analysis with the added benefit of enhanced column lifetime and reduced source maintenance compared to the normal large volume injection approach.

References
1. Organtini K, Cleland G, Rosnack K. Large Volume Direct Injection Method for the Analysis of Perfluorinated Alkyl Substances (PFAS) in Environmental Water Samples in Accordance with ASTM 7979-17. Waters Application Note 720006329, June 2018.
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3. ASTM D7979-17, Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), ASTM International, West Conshohocken, PA, 2017, www.astm.org

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