Improved Sensitivity for the Detection of Per- and Polyfluorinated Alkyl Substances in Environmental Water Samples Using a Direct Injection Approach on Xevo™ TQ Absolute

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This is an Application Brief and does not contain a detailed Experimental section.

Abstract

Detection requirements for per- and polyfluorinated alkyl substances (PFAS) have been getting more challenging as regulations to protect consumers continue to be created and updated for various types of water. This simple method using direct injection for PFAS analysis requires a highly sensitive mass spectrometer to reach necessary performance criteria. The enhanced negative ion sensitivity of the Xevo TQ Absolute Tandem Quadrupole Mass Spectrometer allows for utilization of the direct injection method for PFAS analysis with a reduced sample injection volume of 10 µL without compromise to method performance. Performance has been shown in four water sample matrices: drinking water, ground water, surface water, and influent wastewater. Method detection limits of 33 compounds (11 carboxylates, 10 sulfonates, 8 precursors, and 4 emerging) were determined to range from 0.8–2.0 ng/L.

Benefits

· Minimal and rapid sample preparation using a dilute and shoot approach to increase laboratory throughput, while also reducing potential sources of sample contamination

· Increased sensitivity to quantify PFAS in environmental water samples using a direct injection approach with

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analysis on the Xevo TQ Absolute

· Reduced sample injection volume enables prolonged column lifetime and source cleanliness while ensuring suitable chromatography

Introduction

Analysis of 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 requirements for method sensitivity have become essential. 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, 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, 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.

Method Information

Samples were prepared using the dilution protocol described in Waters application Note 720006329.[1] A method detection limit (MDL) study was performed following the EPA procedure EPA 821-R-16-006 using 10 replicates in

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reagent water.[3] Analysis was performed on ACQUITY™ UPLC I-Class PLUS System FTN with PFAS Analysis Kit coupled to Xevo TQ Absolute. Mobile Phases were (A) 2 mM ammonium acetate in water and (B) 2 mM ammonium acetate in methanol using the following 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

Mass spectrometer settings used can be found in Waters application Note 720006329.

Results and Discussion

The calculated Method Detection Limits (MDLs) are 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.

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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.

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™ for quantitation software platform allows for easy visual representation and review of data. For this analysis, 50% deviation was allowed near the LLOQ, and 30% deviation was allowed for the remainder of the curve. These values are used as examples of typical data quality allowances found in EPA PFAS regulatory methods.
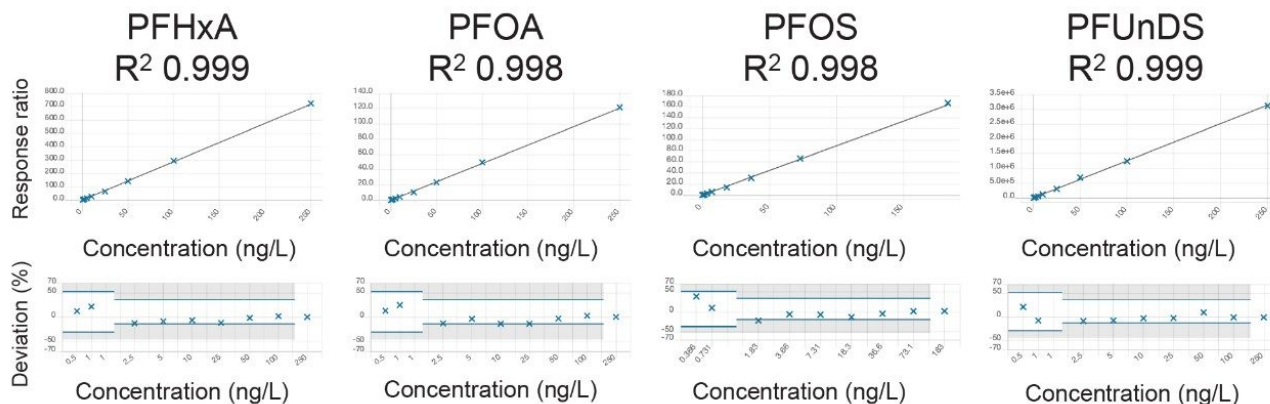
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Figure 1. Calibration data of four PFAS compounds demonstrating calibration curve linearity and calibration deviation.

A variety of water samples ranging in complexity were evaluated using this method on the Xevo TQ Absolute 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. Additionally, Figure 3 demonstrates the stability of the method performance in the 10 ng/L CCV sample that was injected seven 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%. Finally, 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.
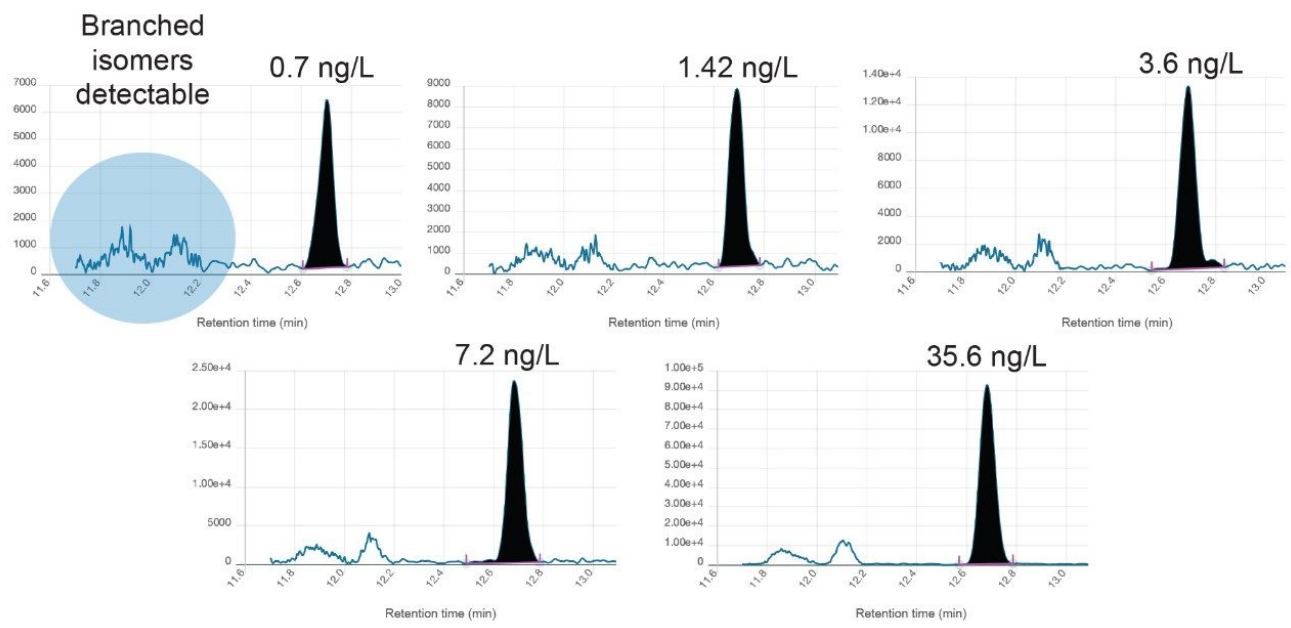
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Figure 2. PFOS in wastewater influent at various spiked concentrations.

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	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. <LLOQ signifies a positive identification, but concentration was not reported as it was below the calibration range.
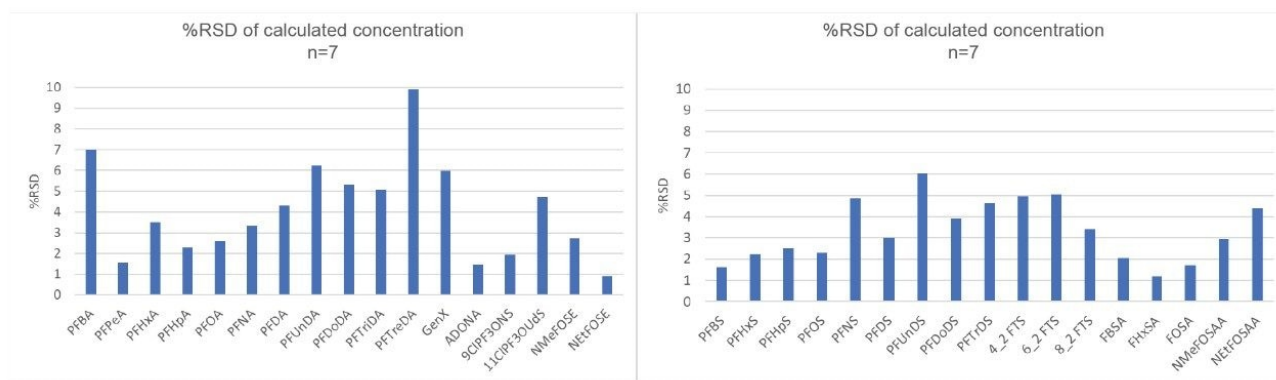

Figure 3. Precision (%RSD) of for calculated concentrations of n=7 injections of 10 ng/L CCV throughout a sample batch of over 120 injections

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Conclusion

The required method detection limits for PFAS have continually been decreasing as regulations to protect consumers from contaminated sources of water continue to be created and updated. The direct injection approach for PFAS analysis has been gaining popularity as a quick and simple option. Not only does this approach require a highly sensitive mass spectrometer to reach these performance criteria, but it also has required large injection volumes to reach the desired detection limits. The enhanced negative ion sensitivity of the Xevo TQ Absolute 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 evaluation of this approach on the Xevo TQ Absolute has been demonstrated 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 these water samples as low as 1.2 ng/L. The combination of the enhanced sensitivity of the Xevo TQ Absolute, 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.

2. Willmer H, Organtini K, Adams S. Routine Determination of Per- and Polyfluorinated Alkyl Substances (PFAS) in Drinking Water by Direct Injection Using UPLC-MS/MS to Meet the EU Drinking Water Directive 2020/2184 Requirements. Waters Application Note 720007413, October 2021.

3. US Environmental Protection Agency. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. EPA 821-R-16–006. December 2016.

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