

# PUSHING PFAS POSSIBILITIES: THE HUNT FOR ULTRA SENSITIVITY TO REACH PPQ EPA HEALTH ADVISORY LEVELS

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## INTRODUCTION

PFAS are well known chemicals with a variety of commercial and consumer uses, characterized by their extreme stability and structural diversity. PFAS are highly persistent and toxic contaminants that accumulate in humans, animals, and the environment. The negative impacts on human health are extensive and continue to be investigated. In addition, PFAS pollution affects ecosystems and generates costs through the need for remediation of polluted soil and water. Some countries impose regulatory or advisory limits on the concentration of various PFAS in drinking, ground, and surface waters.

Detection requirements for PFAS have been getting more challenging as advisory and regulatory limits continue to be created and updated. In June 2022, the US EPA tightened its health advisory levels (HALs) in drinking water from 70 ng/L to 0.004 ng/L for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). The recommendation is 0.004 ng/L (part per trillion, ppt) for PFOA and 0.02 ng/L for PFOS, both of which are categorized as interim levels. These levels are dramatically more stringent than the 70 ng/L (ppt) total that the EPA recommended in 2016. Additionally, final HALs were set for perfluorobutane sulfonic acid (PFBS) at 2000 ng/L and hexafluoropropylene oxide dimer acid (HFPO-DA; commonly referred to as GenX) at 10 ng/L. The near zero PFOA and PFOS levels pose analytical challenges regarding instrument sensitivity and sample preparation conditions to limit contamination.

This work focused on reaching the more stringent limits of the EPA HALs, detailing a PFAS analytical workflow approach using SPE extraction with Oasis™ WAX for PFAS Cartridge to enrich water samples with analysis performed on a Waters™ ACQUITY™ Premier UPLC™ System and Xevo™ TQ Absolute MS with data analysis using waters\_connect™ for Quantitation software.

## METHODS

### Sample Prep

Samples were prepared through SPE enrichment using Oasis WAX for PFAS SPE cartridges following the procedure outlined in Figure 1, resulting in a 500x enrichment of the sample. Best practices to reduce contamination during the sample preparation were followed.<sup>1</sup>

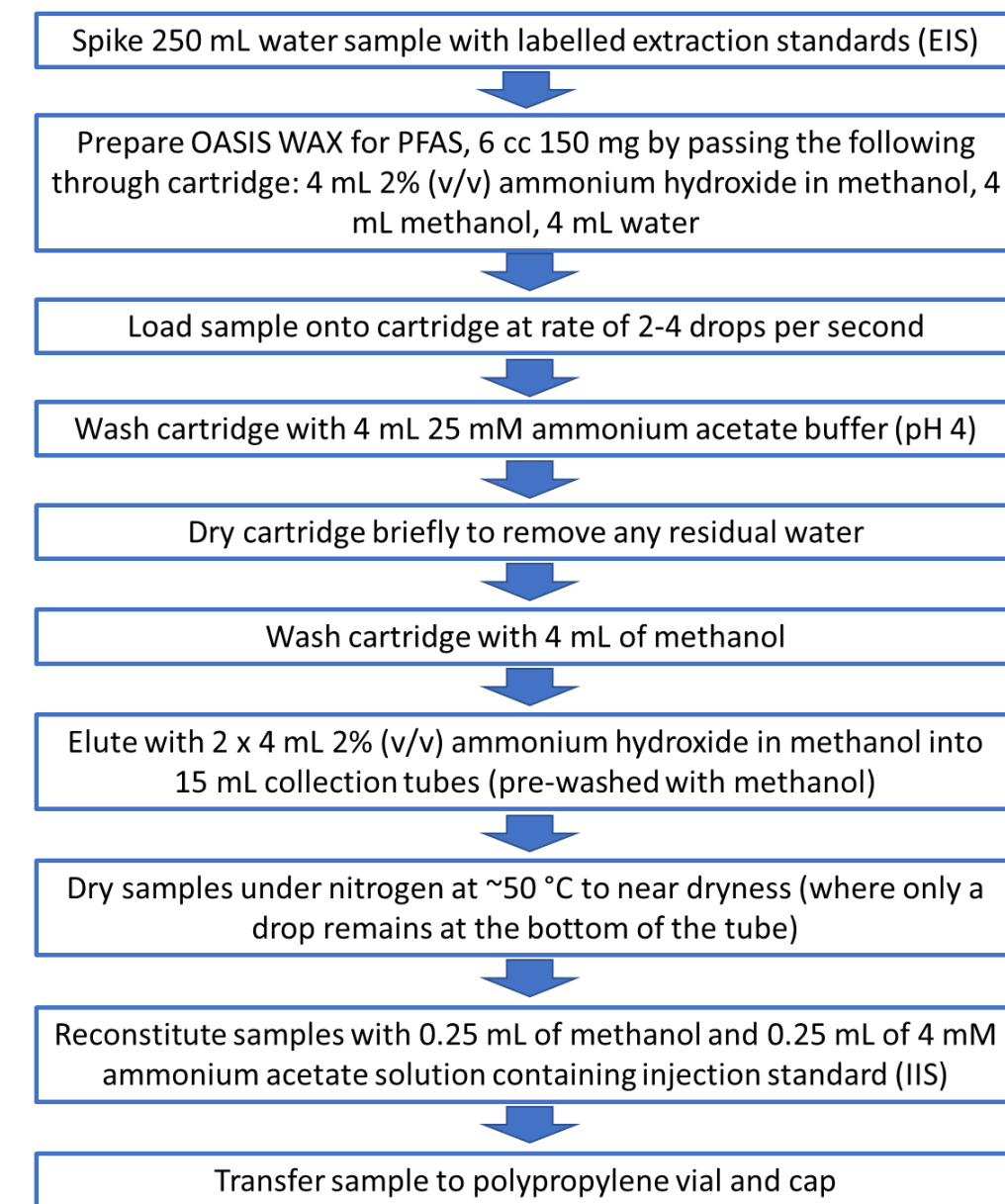


Figure 1. Full SPE method used for extracting drinking water samples using Oasis WAX for PFAS cartridges.

Mobile Phase A: Water + 2 mM ammonium acetate

Mobile Phase B: Methanol + 2 mM ammonium acetate

Gradient:

Time (min)	%A	%B	Curve
0	95	5	initial
1	75	25	6
6	50	50	6
13	15	85	6
14	5	95	6
17	5	95	6
18	95	5	6
22	95	5	6

### LC-MS/MS Conditions

LC System: ACQUITY Premier BSM UPLC System with FTN fitted with PFAS Kit

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

Column Temp: 35°C

Sample Temp: 10°C

Injection Volume: 10 µl

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

Instrument sensitivity of the Xevo TQ Absolute MS was evaluated on two different instruments located in two different laboratories. Laboratory 1 was located in Wilmslow, United Kingdom and Laboratory 2 was located in Milford, Massachusetts, United States. The Limit of Quantitation (LOQ) for each laboratory as well as the signal:noise (S:N) at the LOQ is listed in Table 1. The LOQ for each compound was well below the minimum reporting level suggested by the EPA guidelines, as well as below the HAL levels (both interim and final), indicating that the Xevo TQ Absolute MS has the sensitivity required for this challenging analysis.

Calibration samples were acquired in the sample range of 0.0005 to 0.08 ng/L (0.25 to 40 ng/L in vial equivalent) with all curves linear over this range, with a correlation coefficient of ≥ 0.992 and residuals within 30%. Figure 2 depicts the calibration curves for all four PFAS across this range.

All four PFAS compounds were absent from all solvent blank injections, indicating the LC-MS/MS system itself, as well as sample vials, were free from PFAS contamination. PFOA, PFOS, and PFBS were detected in extraction blanks at varying levels indicating introduction of these compounds during the sample preparation step. The PFOA contamination of the extraction blank represented approximately 21% of the 0.004 ng/L sample spike, while PFOS was approximately 4% of the 0.02 ng/L sample spike. PFBS contamination was also compared to the 0.02 ng/L sample spike, and was 8% of that response. Since the HAL for PFBS is orders of magnitude higher than this sample spike, this extraction blank contamination can be considered negligible. An overlay of the chromatograms for all four compounds in the solvent blank, extraction blank, and extracted sample can be seen in Figure 3. According to data quality guidelines in EPA methods, such as those found in EPA 537.1 and 533, the contamination levels are significantly below the 1/3 MRL requirement.<sup>2,3</sup>

Sample preparation method performance was evaluated in the 0.004 and 0.02 ng/L sample spikes by their calculated concentrations and recovery values, with results listed in Table 2. The average recovery and %RSD values demonstrate excellent method accuracy and repeatability. Recovery for each compound at both concentration levels ranged from 90 to 111%, and RSD was within the range of 2 to 13%. This lends high confidence in reporting results for drinking water samples at these challenging trace levels.

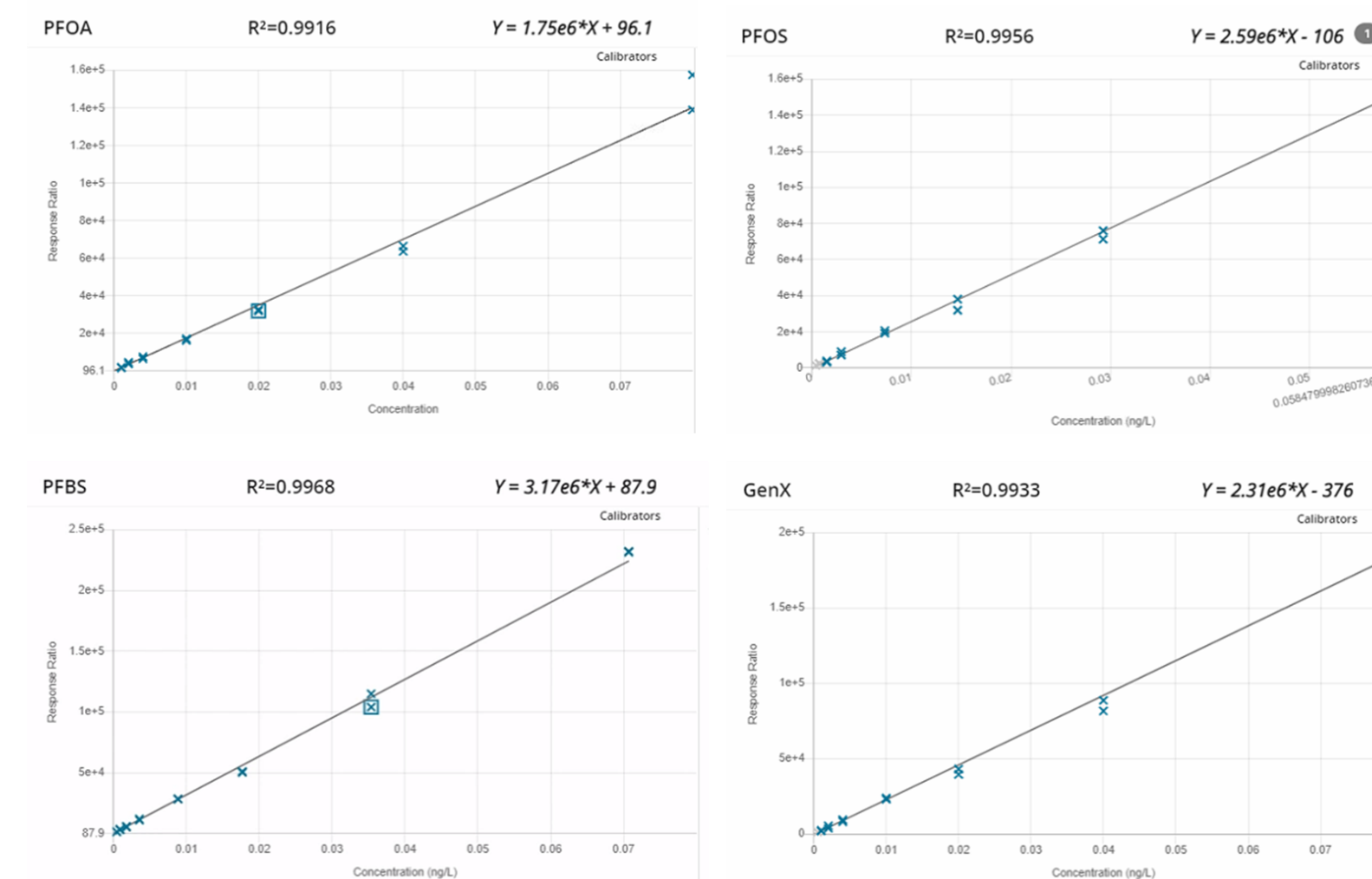


Figure 2. Calibration curves for PFOA, PFOS, PFBS, and GenX on the Xevo TQ Absolute.

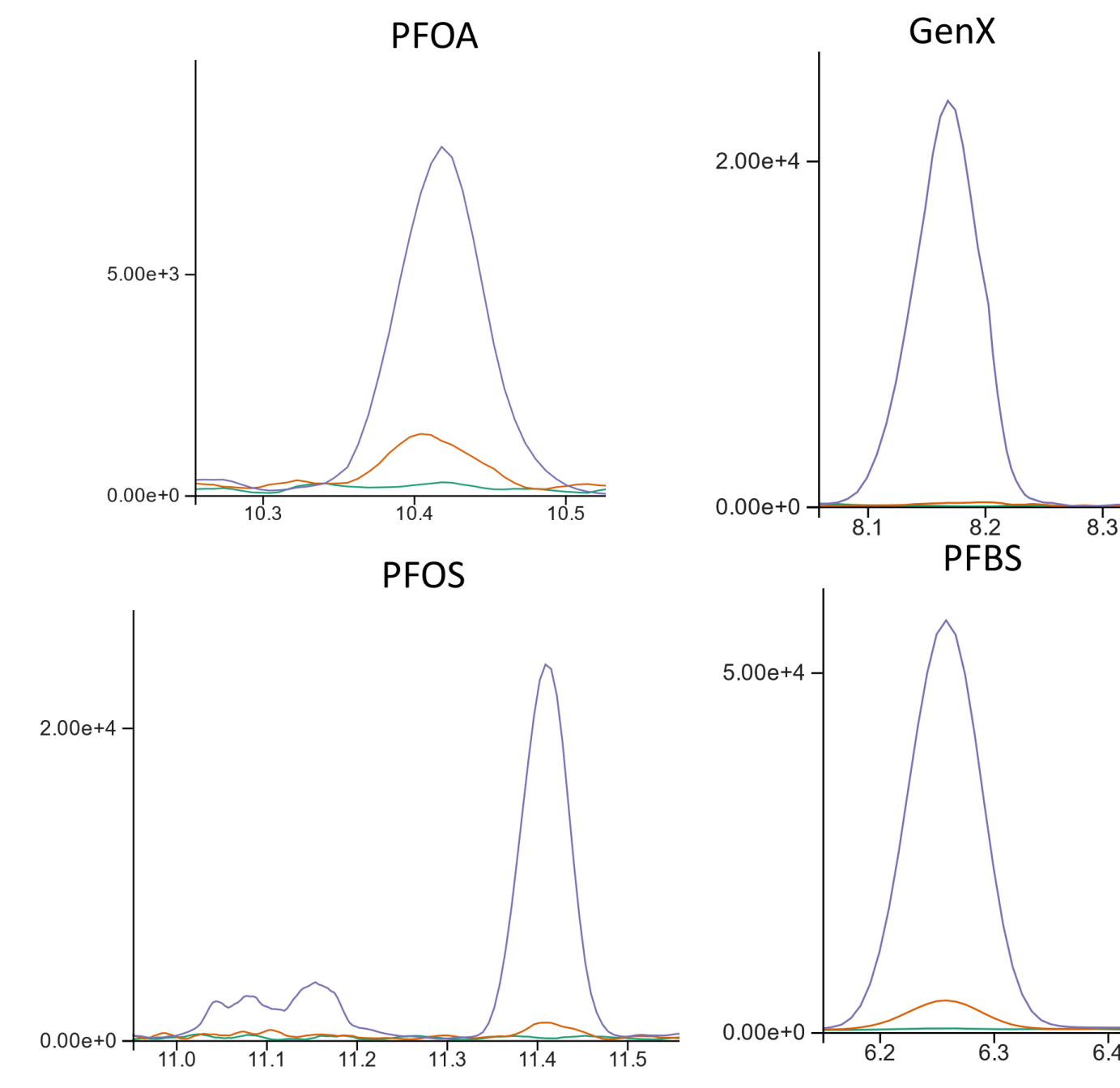


Figure 3. Overlaid chromatograms of PFOA (0.004 ng/L), PFOS (0.02 ng/L), PFBS (0.02 ng/L), and GenX (0.02 ng/L) demonstrating spiked sample extracts (blue) to extraction blanks (orange) and solvent blanks (green).

Compound	Laboratory 1 LOQ ng/L	Laboratory 1 S:N of LOQ	Laboratory 2 LOQ ng/L	Laboratory 2 S:N of LOQ	EPA HAL ng/L	Interim minimum reporting level ng/L
PFOA	0.001	10	0.001	10	0.004 (interim)	4
PFOS	0.001	12	0.001	27	0.02 (interim)	4
PFBS	0.0009	24	0.002	27	2,000	3
HFPO-DA (GenX)	0.004	21	0.004	10	10	5

Table 1. Limit of quantitation (LOQ) and signal:noise (S:N) for each PFAS determined in both laboratories using two different Xevo TQ Absolute MS systems.

0.004 ng/L spike				
	Expected concentration (ng/L)	Average calculated concentration (ng/L)	% RSD	Average % recovery
PFOA	0.0040	0.0042	5	105
PFOS	0.0029	0.0030	5	103
PFBS	0.0035	0.0032	2	90
GenX	0.0040	0.0037	13	91
0.02 ng/L spike				
	Expected concentration (ng/L)	Average calculated concentration (ng/L)	Standard deviation (ng/L)	Average % recovery
PFOA	0.020	0.022	9	111
PFOS	0.015	0.014	6	94
PFBS	0.018	0.017	3	96
GenX	0.020	0.021	10	107

Table 2. Average calculated concentration, %RSD and average percent recovery (n=3) of the HAL PFAS in water samples spiked at 0.004 and 0.02 ng/L.

## CONCLUSION

- With the use of the enhanced negative ion mode sensitivity of the Xevo TQ Absolute along with sample enrichment gained by sample extraction using Oasis WAX SPE cartridges, this work has demonstrated that a typical laboratory can reach the HAL requirements from the EPA, including the interim sub-ppt levels for PFOA and PFOS
- Additional or special resources were not required outside the normal range of an analytical prep shared-space laboratory.
- The challenging factor in this analysis was demonstrated to be cleanliness during sample preparation to limit the amount of PFAS contamination during this step.
- With focus on laboratory practices and sample handling, contamination can be kept to a minimum so that it does not significantly impact the reported results.
- Of the four PFAS with assigned HALs, PFOA proved to be the compound that had the most background contamination, but was still within typical data quality guidelines.
- The SPE method using Oasis WAX cartridges was shown to be accurate and repeatable with excellent recoveries and % RSD of replicates.
- The full workflow presented in this study demonstrates it is possible to reliably detect challenging trace levels of PFAS, in the ppq range, in drinking water samples.

### References

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2. Shoemaker, J and Tetterhorst, D. Method 537.1: Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, 2018.
3. Rosenblum, L and Wendelken, S. Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water, Standards and Risk Management Division, 2019.