Pushing PFAS Possibilities: The Hunt For Ultra Sensitivity To Reach PPQ EPA Health Advisory Levels

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INTRODUCTION

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). This work focused on reaching these more stringent limits using Oasis™ WAX SPE Cartridges for PFAS analysis to enrich water samples, with analysis being performed on a Waters ACQUITY™ Premier UPLC™ System and Xevo™ TQ Absolute MS with data analysis using waters_connect™ for Quantitation.

SAMPLE PREPARATION

Samples were prepared through SPE enrichment using Oasis WAX SPE Cartridges for PFAS analysis 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.

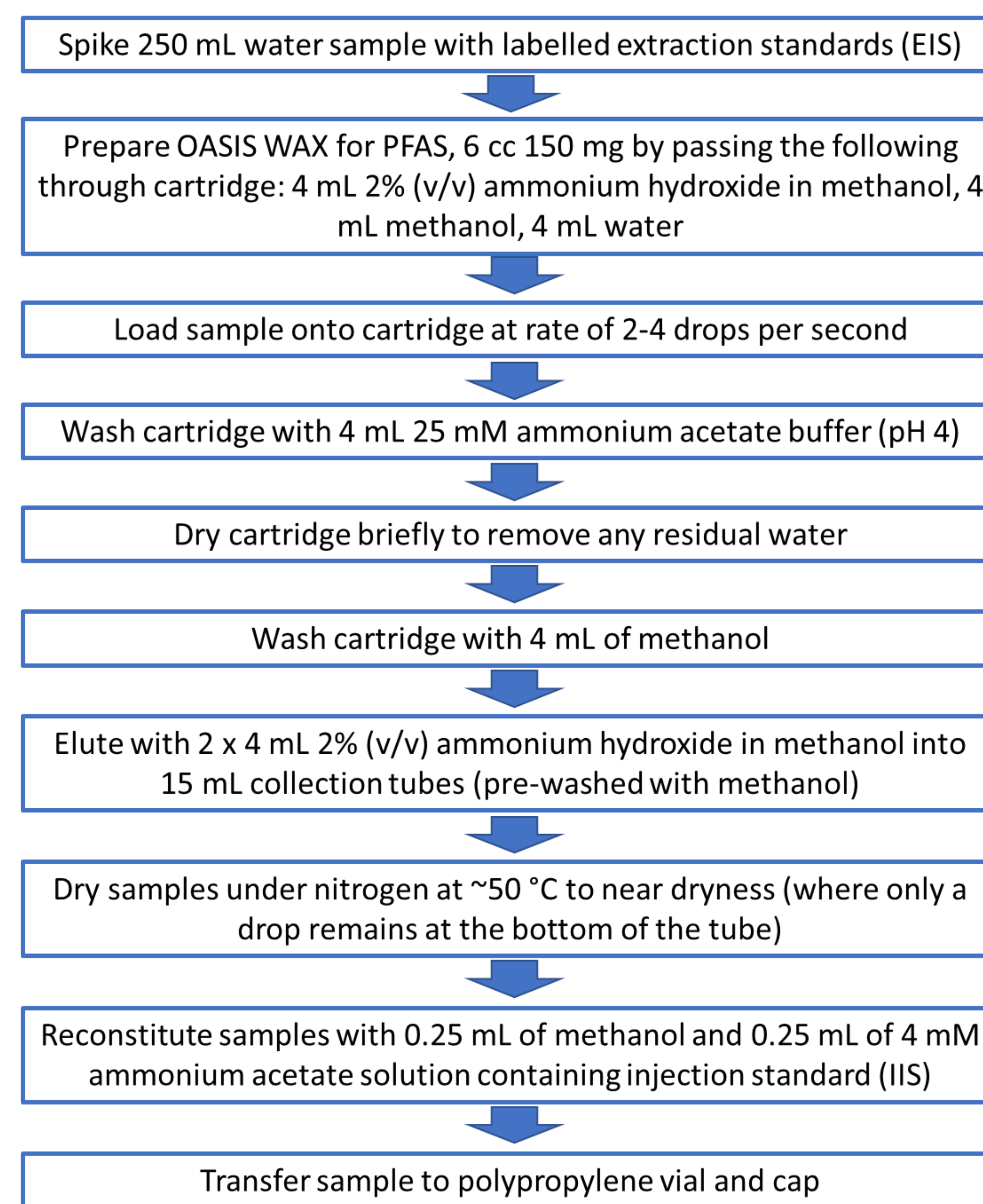Waters PFAS Solution Installation Kit: PN 176001744

Figure 1 flowchart:
- Spike 250 mL water sample with labelled extraction standards (EIS)
- Prepare OASIS WAX for PFAS, 6 cc 150 mg by passing the following through cartridge: 4 mL 2% (v/v) ammonium hydroxide in methanol, 4 mL methanol, 4 mL water
- Load sample onto cartridge at rate of 2-4 drops per second
- Wash cartridge with 4 mL 25 mM ammonium acetate buffer (pH 4)
- Dry cartridge briefly to remove any residual water
- Wash cartridge with 4 mL of methanol
- Elute with 2 x 4 mL 2% (v/v) ammonium hydroxide in methanol into 15 mL collection tubes (pre-washed with methanol)
- Dry samples under nitrogen at ~50 °C to near dryness (where only a drop remains at the bottom of the tube)
- Reconstitute samples with 0.25 mL of methanol and 0.25 mL of 4 mM ammonium acetate solution containing injection standard (IIS)
- Transfer sample to polypropylene vial and cap

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

LC/MS-MS METHOD

LC System	ACQUITY Premier UPLC BSM System fitted with the PFAS Analysis Kit
Column	ACQUITY Premier BEH™ C_{18} 2.1 x 100 mm, 1.7 µm Column
Mobile Phase A	Water with 2 mM ammonium acetate
Mobile Phase B	Methanol with 2 mM ammonium acetate
Software	waters_connect for Quantitation
Injection Vol	10 µL
Column Temp	35°C
Sample Temp	10°C

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

MS System	Xevo TQ Absolute Mass Spectrometer, ESI-
Capillary Voltage	0.5 kV
Desolvation Temp	350°C
Desolvation Gas Flow	900 L/hr
Cone Gas Flow	150 L/hr
Source Temp	100°C

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Table 1. Instrument configuration, ionization mode, and chromatographic conditions.

RESULTS AND DISCUSSION

Instrument sensitivity of the Xevo TQ Absolute MS was evaluated on two different instruments located in two different laboratories.

Laboratory 1: Wilmslow, United Kingdom

Laboratory 2: 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 2.

The LOQ for each compound was well below the minimum reporting level suggested by the EPA guidelines, as well as below the HALs (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%. Fig. 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. An overlay of the chromatograms for all four compounds in the solvent blank, extraction blank, and extracted sample can be seen in Figure 3. The contamination levels are significantly below the 1/3 minimum reporting level (MRL) requirement specified in the data quality guidelines in EPA methods, such as those found in EPA 537.1 and 533.

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 3. 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.
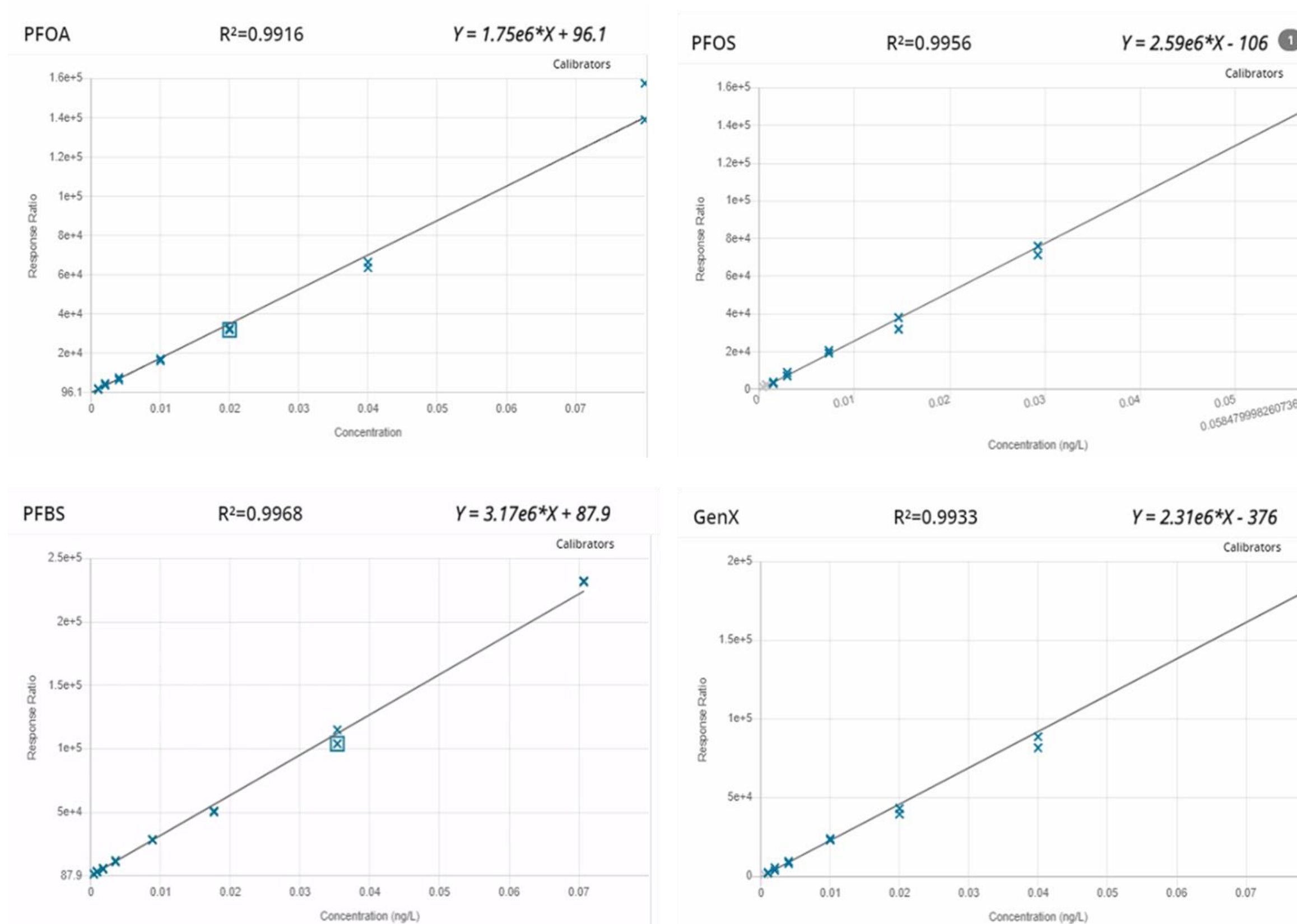
Figure 2 (calibration curves):
- PFOA: R²=0.9916, Y = 1.75e6*X + 96.1
- PFOS: R²=0.9956, Y = 2.59e6*X - 106
- PFBS: R²=0.9968, Y = 3.17e6*X + 87.9
- GenX: R²=0.9933, Y = 2.31e6*X - 376

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

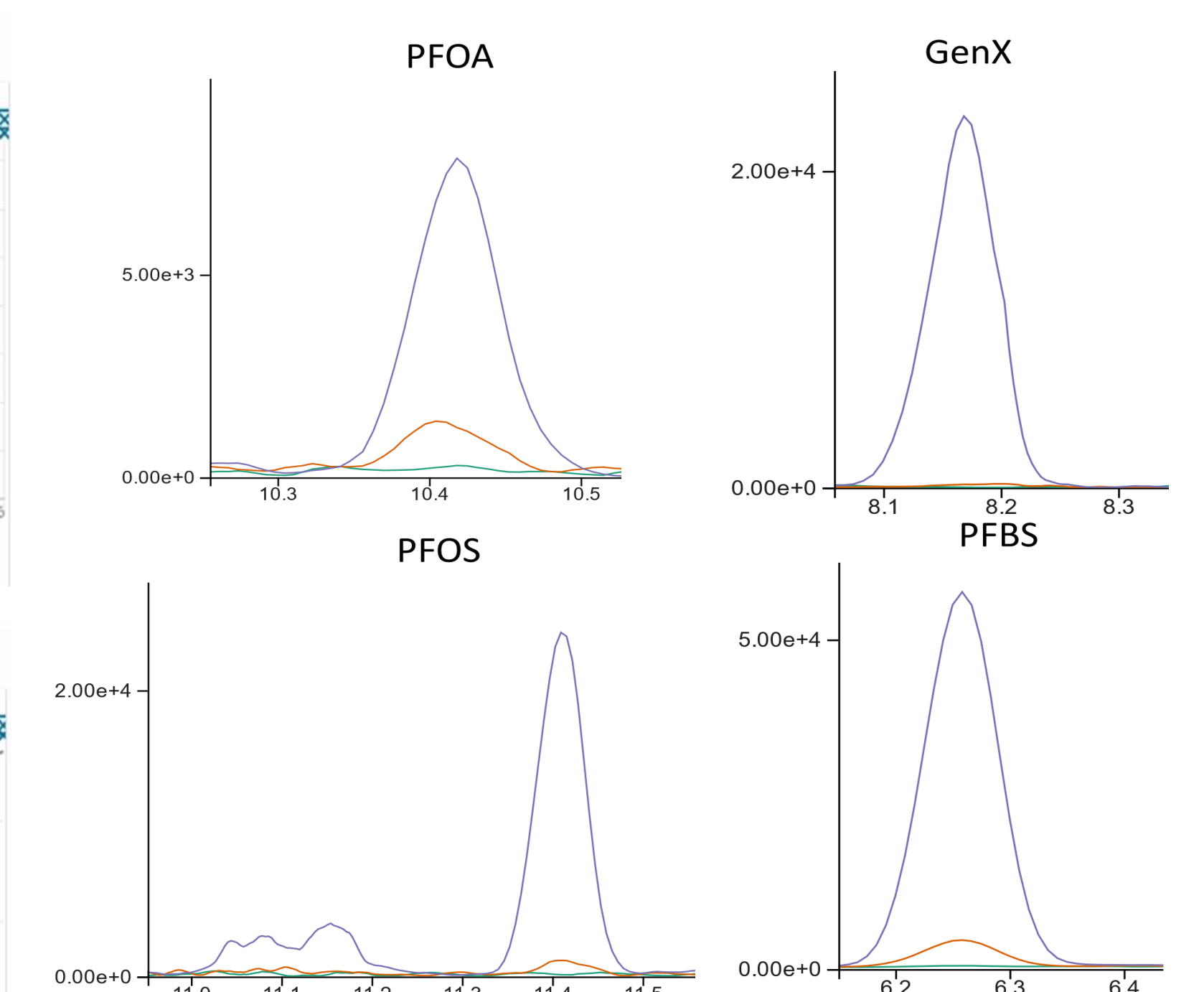**Figure 3 (overlaid chromatograms): PFOA, GenX, PFOS, PFBS**

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	Lab 1 LOQ ng/L	Lab 1 S/N of LOQ	Lab 2 LOQ ng/L	Lab 2 S/N of LOQ	EPA HAL ng/L	Interim MRL 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	2000	3
HFPO-DA (GenX)	0.004	21	0.004	10	10	6

Table 2. 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 3. 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.

CONCLUSIONS

- With the use of the enhanced negative ion mode sensitivity of the Xevo TQ Absolute MS along with sample enrichment gained by sample extraction using Oasis WAX SPE Cartridges for PFAS analysis, 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.

- By focusing 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 SPE Cartridges for PFAS analysis 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.

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