ROUTINE EPA 1633 PFAS ANALYSIS WITH A NOVEL SLOTTED BANDPASS ION GUIDE TO IMPROVE SIGNAL RESPONSE ROBUSTNESS

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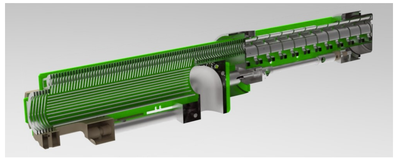
INTRODUCTION

As awareness grows around the environmental and health impacts of per- and polyfluoroalkyl substances (PFAS), regulatory pressure continues to intensify globally.

The US EPA Method 1633A[1] has become a critical protocol for the quantitation of 40 PFAS compounds in diverse environmental matrices, including non-potable water, soils, biosolids, and tissues.

Although the method describes a solid phase extraction (SPE) clean-up step for all sample types, these matrices still contain co-extractive interferents when introduced into an LC-MS/MS system, which can contaminate the system and degrade method performance over time.

Here we describe how the StepWave™ XR Ion Guide, a novel slotted bandpass ion guide, within the Xevo™ TQ Absolute XR Mass Spectrometer, can be integrated into a typical PFAS workflow to enhance signal robustness, while preserving sensitivity and speed, thereby boosting method reliability.



1 x	**8 x Solvent calibration standards**
3 x	Methanol solvent
	5 x Biosolid sample extract, 1/10 dilution
	Methanol solvent
	5 x Leachate sample extract
	Methanol solvent
	Solvent calibration QC
	5 x River water spiked sample extract
	Methanol solvent
	5 x Biosolid sample extract, 1/10 dilution
	Methanol solvent
	Solvent calibration QC
	5 x Leachate sample extract
	Methanol solvent
	5 x River water spiked sample extract
	Methanol solvent
	Solvent calibration QC

Figure 1. Analytical sequence of a single batch (lasting 128 injections and 25 hours) used during the robustness study.

METHODS

Sample Preparation

River water (250 mL) was collected in Scotland, UK from the River Tay. Biosolid (0.5 g domestic sludge NIST 2781) and landfill leachate (25 mL LGC 6177) were both purchased as reference materials.

Extraction and SPE clean-up were carried out as outlined previously[2,3]. River water was spiked with native and internal standards after screening identified that PFAS were not detected. Biosolid and landfill leachate both had PFAS present and were only spiked with internal standards. 2 replicates were extracted, combined and then diluted 1 in 10 with methanol before analysis for the biosolid. For both the landfill leachate and spiked river water samples, 5 replicates of each were extracted and combined before analysis.

Analysis Sequence

The sequence of a single batch is shown in Figure 1 and shows the order and number of injections. Linear, 1/x weighted calibration curves were plotted weekly. The data quality guidelines outlined in EPA 1633A were used to demonstrate capability. Pre-emptive routine maintenance was performed with the cone cleaned and columns changed monthly (approx. every 3000 injections). Other maintenance was not performed, and the system was not vented for the entirety of the study apart from an unscheduled electrical power cut after 6278 injections.

LC-MS/MS Conditions

Separation was performed on an ACQUITY™ Premier System with Binary Solvent Manager and Flow-Through Needle. 2 µL injections were made onto an ACQUITY Premier BEH™ C18 Column 2.1 x 50 mm, 1.7 µm analytical column held at 35 ºC with an Atlantis™ Premier BEH C18 AX Column 2.1 x 50 mm, 5 µm isolator column. A stepped gradient at 0.3 mL/min composing 2 mM aqueous ammonium acetate and 2 mM ammonium acetate in acetonitrile (5% to 95%) over 7 minutes was used to elute the column.

A Xevo TQ Absolute XR Tandem Quadrupole Mass Spectrometer in negative ion electrospray ionization and multiple reaction monitoring mode was used for detection. The capillary was operated at 0.5 kV with a source temperature of 100 ºC, a nitrogen desolvation gas temperature of 350 ºC and flow rate of 900 L/hr and a nitrogen cone gas flow rate of 150 L/hr. Argon was used as the collision gas with MRM parameters that have been previously published[2].

Data acquisition, processing and review were performed using waters_connect™ for Quantitation Software.

RESULTS AND DISCUSSION

QC Performance

Method performance was evaluated every 10 sample injections to ensure that the weekly calibration of the method was stable. Figure 2 shows the trueness plots with the ion ratio %RSDs for GenX, L-PFHxS, L-PFOS, PFBS, PFNA and PFOA with a tolerance of ± 30% set from the assigned concentration level (0.1 - 0.2 ng/mL). QC measured concentrations and ion ratios were within the set tolerances across 12 weeks and more than 9000 injections with no unscheduled downtime. This illustrates the reliability of the Xevo TQ Absolute XR for PFAS analysis using a weekly calibration routine.

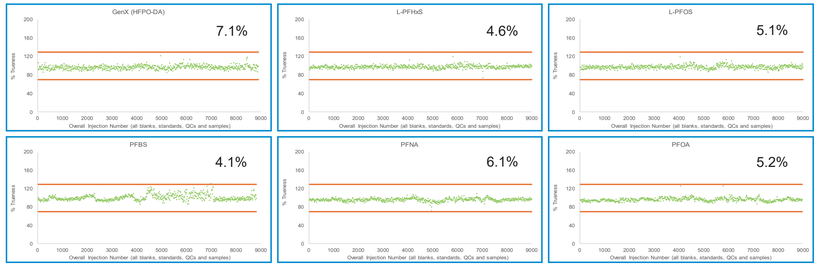


Figure 2. QC Plots and ion ratio %RSDs from weekly calibrations for GenX, L-PFHxS, L-PFOS, PFBS, PFNA and PFOA.

Spiked River Water Results

River water spiked samples were repeatedly measured across the robustness study. Figure 3 shows the trueness plots for GenX, L-PFHxS, L-PFOS, NFDHA, PFDoDS and PFNA with a tolerance of ± 30% set from the spiked concentration level. Trueness was within the set tolerance across 12 weeks and more than 9000 injections with no unscheduled downtime. This demonstrates the overall measurement reliability of the Xevo TQ Absolute XR for PFAS analysis in aqueous matrices.

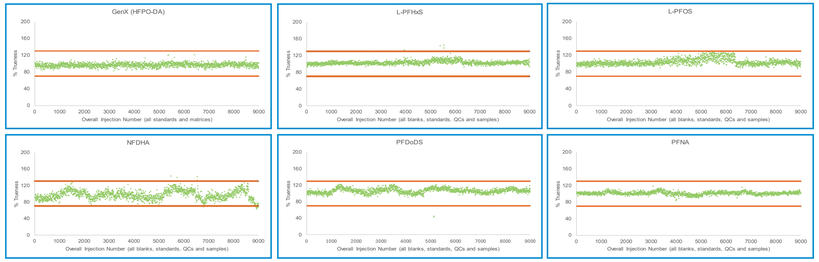


Figure 3. Trueness plots for GenX, L-PFHxS, L-PFOS, NFDHA, PFDoDS and PFNA in spiked river water.

Biosolid Results

The certificate of analysis for the biosolid sample stated reference values for different PFAS. One example was for L-PFHxS, where the measured values in the biosolid extracts over the course of the study are plotted in Figure 4. The mean measured value was 8.78 µg/kg with a %RSD of 7.2% across 12 weeks and more than 9000 injections with no unscheduled downtime. This compared very favorably with the certified value of 9.39 µg/kg. Table 1 lists the mean measured values and the %RSDs for the six PFAS compared to the certified value and range.

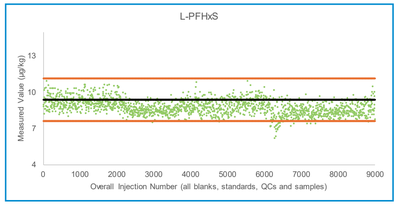


Figure 4. Measured value of L-PFHxS in the biosolid extracts (Black = assigned value, Orange = upper and lower uncertainty from the CoA).

PFAS	Measured value (µg/kg)	%RSD	Certified value (µg/kg)	Certified value range (µg/kg)
FOSA	5.61	3.3	6.31	5.34 – 7.28
L-PFHxS	8.78	7.2	9.39	7.63 – 11.15
L-PFOS	232	8.6	225	184 – 266
PFHpA	8.64	6.8	7.96	6.46 – 9.46
PFOA	26.6	3.4	28.5	25.2 – 31.8

Table 1. Mean measured values and %RSDs of PFAS in the biosolid extracts and how they compare to the certified values.

Landfill Leachate Results

Several incurred residues were detected in the landfill leachate sample. Figure 5 shows one example, PFOA, where the mean calculated concentration was 2.52 ng/mL with a %RSD of 2.7% across 12 weeks and more than 9000 injections with no unscheduled downtime. A tolerance of ± 30% was set from the mean of the first 10 calculated concentrations. Table 2 lists the mean calculated concentrations and the %RSDs for the PFAS in the landfill leachate sample.

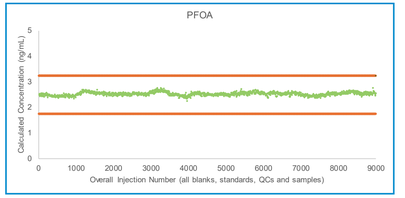


Figure 5. Calculated concentration of PFOA in landfill leachate extracts.

PFAS	Calculated concentration (ng/mL)	Calculated concentration %RSD	Mean ion ratio	Ion ratio %RSD
L-PFHxS	0.76	2.3	0.58	3.6
L-PFOS	0.29	3.5	0.63	8.8
PFBS	7.43	4.6	0.26	5.0
PFHpA	1.37	3.1	0.49	3.4
PFHxA	5.05	5.4	0.11	7.5
PFOA	2.52	2.6	0.62	2.8
PFPeA	1.54	4.2	0.03	8.0

Table 2. Mean calculated concentrations, mean ion ratios and %RSDs for the PFAS reported in the landfill leachates extract.

CONCLUSION

- **StepWave XR Ion Guide within the Xevo TQ Absolute XR Mass Spectrometer was introduced into a typical PFAS workflow and shown to maintain method reliability for extended time periods.**
- **Xevo TQ Absolute XR MS provided maximal system uptime for PFAS analysis across 12 weeks and more than 9000 injections with no unscheduled downtime.**
- **Reliable calculated concentrations were maintained for PFAS at relevant levels in extracts of river water, biosolid and landfill leachate with trueness in the range 70-130% and %RSDs of <8.8%.**
- **Seamless batch review and long-term calibration management using waters_connect for Quantitation Software accelerated data validation workflows.**

References

1. US Environmental Protection Agency, EPA Method 1633A, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. Dec 2024.
2. Organtini KL, Rosnack KJ, Plummer C, Hancock PM, Burt O. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Accordance with EPA 1633 Part 2: Analysis of Aqueous Matrices. Waters Application Note 720008143. Dec 2023.
3. Organtini KL, Rosnack KJ, Plummer C, Hancock PM, Burt O. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Accordance with EPA 1633 Part 3: Analysis of Soil and Tissue. Waters Application Note 720008230. Feb 2024.

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