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Single Quadrupole LC-MS with Line-Shape Calibration Enhancement as an Economical Alternative for PFAS Screening

WP-261

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1. Overview

An accurate mass, single quadrupole liquid chromatography mass spectrometry (SQ-LCMS) method was developed to facilitate screening environmentally relevant Per- and polyfluoroalkyl substances (PFAS)

2. Introduction

PFAS are ubiquitous and enduring contaminants that have harmful impacts on the environment and public health. Analysis of non-volatile PFAS is commonly performed by triple quadrupole liquid chromatography tandem mass spectrometry (TQ-LCMS); the ability to screen PFAS using SQ-LCMS provides a novel and economical alternative for these laboratories. SQ-LCMS is less selective compared to TQ-LCMS; therefore, accurate mass determination through line-shape calibration is a powerful technique for improving compound confirmation.

3. Method

The 40 PFAS targets and 31 internal standards were diluted to match EPA Method 1633A (EPAM1633A) analysis[1]. Neat standards were analyzed from 0.2-1560 ppb in-vial. Cerno Bioscience MassWorks was used to improve mass accuracy. Multiple calibrations were used with differing criteria to evaluate efficacy using the new Target Analysis function.

Table 1. HPLC and MS acquisition parameters

Nexera XR			LCMS-2050	
Analytical Column:		Shim-pack Scepter C18-120, 3 μm; 2.1×50 mm	Ionization Type:	ESI
Delay Column:		Shim-pack Scepter C18-120, 3 μm; 2.1×100 mm	Desolvation Temp:	250 °C
Mobile Phase	A:	2 mM Ammonium acetate in water	DL Temp:	200 °C
	B:	Acetonitrile	Nebulizing Gas:	2.0 L/min
Flow rate:		0.4 mL/min	Heating Gas:	7.0 L/min
Oven temp (°C):		40 °C	Probe Position:	+2 mm
Injection volume:		5 μL	Interface Voltage:	-0.5 kV

4. Results and Discussion

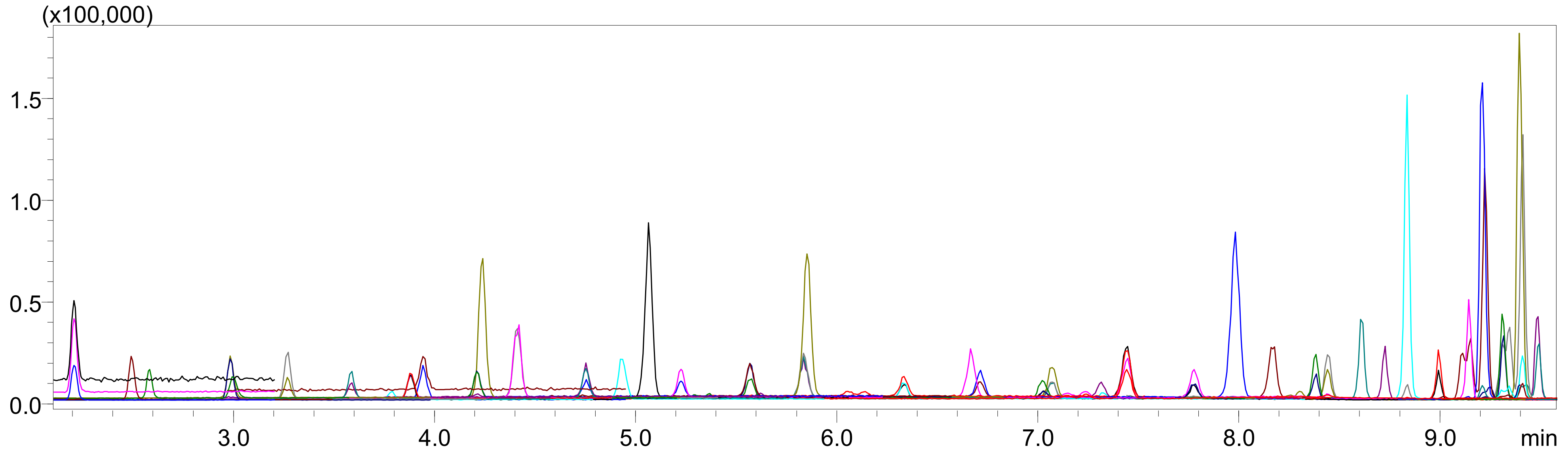

Figure 1. Chromatogram for all analytes at the mid-range calibration standard (1.25-62.4 ppb).

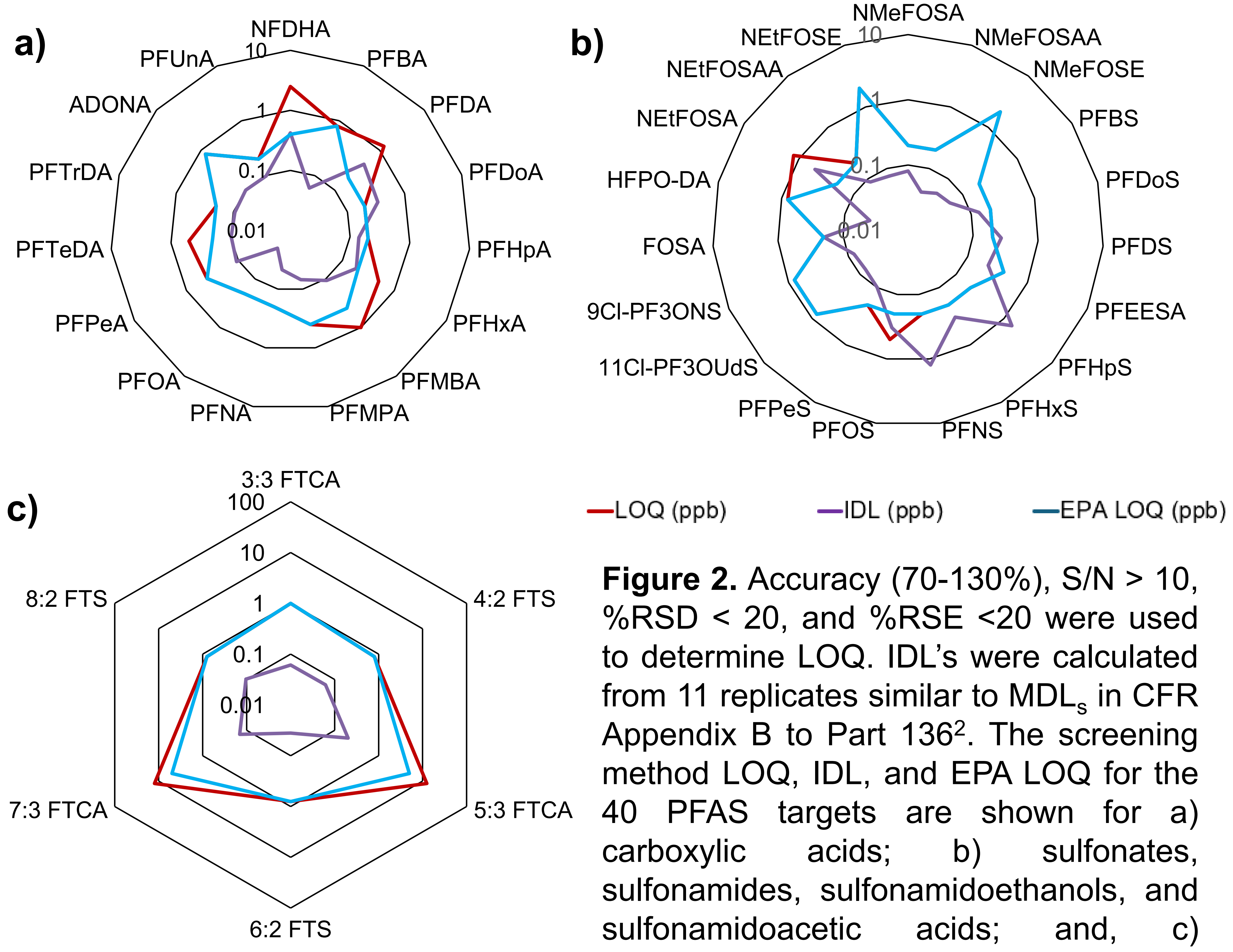

Figure 2. Accuracy (70-130%), S/N > 10, %RSD < 20, and %RSE <20 were used to determine LOQ. IDL's were calculated from 11 replicates similar to MDL_s in CFR Appendix B to Part 136[2]. The screening method LOQ, IDL, and EPA LOQ for the 40 PFAS targets are shown for a) carboxylic acids; b) sulfonates, sulfonamides, sulfonamidoethanols, and sulfonamidoacetic acids; and, c) fluorinated telomer acids and sulfonates.

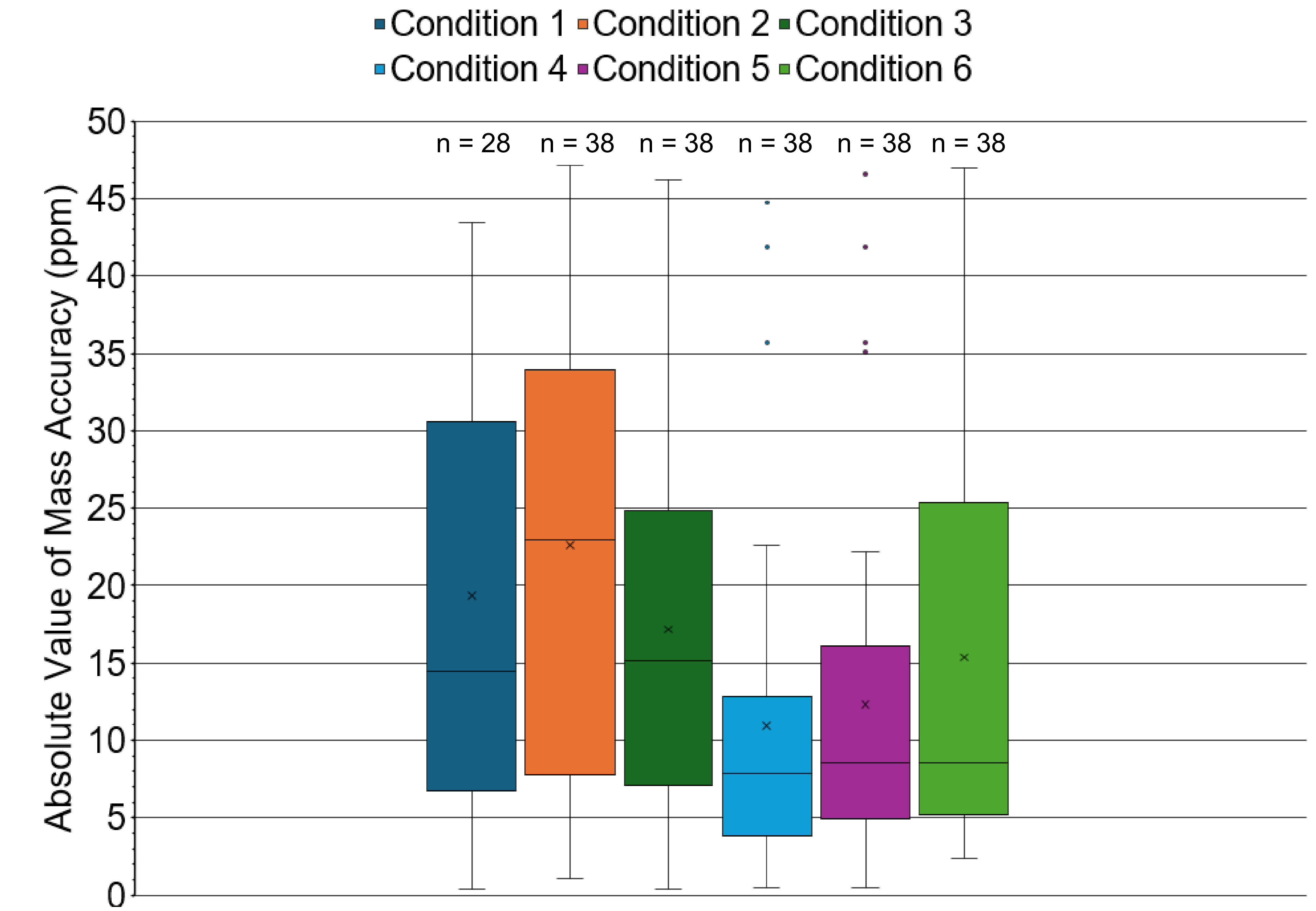

Figure 3. Mass accuracy distribution for the highest calibration standard (62.5-1560 ppb). Compounds with low S/N and mass accuracy ≤50 ppm were not identified. The differing criteria and compounds used for analysis were as follows: **Condition 1** – Sigma ESI Tune mix; **Condition 2** – Condition 1 & benzenesulfonamide; **Condition 3** - 7 internal standards with mass accuracy ≤ 20 mDa **; Condition 4** – Target PFAS with sufficient S/N; **Condition 5** – Target PFAS with mass accuracy ≤ 20 mDa and spectral accuracy ≥ 90%; and, **Condition 6** – Target PFAS with mass accuracy ≤ 10 mDa and spectral accuracy ≥ 95%.

5. Conclusion

- Effective screen for regulated PFAS for SQ-LCMS analysis with low LOQs comparable to EPA.
- Utilizing a calibration with more compounds (Condition 4) resulted in the best overall mass accuracies.
- Target Analysis in MassWorks enabled accurate mass determination for most PFAS by SQ-LCMS.

6. Reference

1. U.S. Environmental Protection Agency, Method 1633A, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. January 2024.
2. CFR Appendix B to Part 136, Title 40 -- Definition and Procedure for the Determination of the Method Detection Limit—Revision 2