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Automated, Sensitive, and Robust Analysis of PFAS in Soil and Fish

Valeria Zerda-Pinto[1]; Ethan R Hain[1]; Brianna Warren[2]; Benedict Liu[2]; Sarah A Monti[1]; Aron Jaffe[1]; Lihini Mendis[1]; Allison Ferranti[1]; Samantha A. Olendorff[1]; Landon A. Wiest[1]; Christopher Gilles[1] ; Alicia Stell[2]; Ruth Marfil-Vega[3]
[1]Shimadzu Scientific Instruments, Columbia, MD; [2]CEM Corporation, Matthews, NC; [3]Shimadzu Corporation, Analytical & Measuring Instruments Division, Japan

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are persistent synthetic chemicals widely used in industry and consumer products, raising environmental and health concerns. To address this, the U.S. EPA has developed standardized methods, including EPA Method 1633A, for monitoring PFAS in various environmental and biological samples. Traditional manual solid sample extraction is time-consuming and prone to variability, highlighting the need for automated solutions to improve efficiency and reproducibility. This work demonstrates the performance of an integrated workflow combining automated solvent extraction for soil and tissue samples using the LCMS-8065XE system for analysis of an extended list of 1633A analytes.

2. Methods

48 native PFAS target compounds were analyzed using 28 extracted internal standards (EIS) and 7 non-extracted internal standards (NIS). Standards were purchased from Cambridge Isotope Labs as PFAS mixtures in methanol. Calibration curves for native PFAS targets were prepared by diluting standards in a solution of methanol with 4% water, 1% ammonium hydroxide, and 0.625% acetic acid. 5 g of soil and Ottawa sand and 2 g of chicken and fish tissue were processed and extracted to a final volume of 5 mL for analysis. EDGE PFAS system (Figure 1) was used for extraction of samples. Figures 2 and 3 describe the extraction process followed for each sample matrix. Analysis was performed by LCMS-8065XE with the instrument conditions listed in Table 1.

Figure 1. EDGE PFAS System for automated extraction

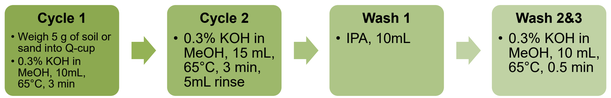

Figure 2. Sample extraction process for tissues samples with the EDGE PFAS system

Figure 3. Sample extraction process for soil and sand samples with the EDGE PFAS system

Millipore Sigma LiChrosolv solvents tested for PFAS methods were utilized for the extraction process. These materials included: MeOH, ACN, Water, formic acid, acetic acid, ammonium solution at 25% and potassium hydroxide. Additionally, LiChrosolv solvents were used as mobile phases for LC-MS analysis.

For each set samples, two low level spikes and one mid level spike were prepared for the analysis. Table 2 breaks down the concentrations in vial for these spikes.

Table 1. LC-MS Conditions for analysis

LC Conditions	**[LC-40 Nexera X3]**
Mobile Phase A	: 2mM ammonium acetate in H_2O
Mobile Phase B	: ACN
Total Run Time	: 12 minutes
Analytical Column	: Shim-pack Scepter C18-120, 50 x 2.1 mm, 3 µm
Delay Column	: Shim-pack Scepter C18-120, 100 x 2.1 mm, 3 µm
Flow Rate	: 0.3 mL/min
Oven Temperature	: 35°C
Injection Volume	: 7 µL
MS Conditions	**[LCMS-8065XE]**
Ionization Mode	: ESI (-)
Acquisition Mode	: MRM
Nebulizing Gas Flow	: 1.1 L/min
Heating Gas Flow	: 15 L/min
Interface Temp	: 225ºC
DL Temperature	: 200°C
Heat Block Temp	: 250°C
Drying Gas Flow	: 5 L/min

Table 2. Spiking concentrations for LLOPR and OPR across all matrices

Compounds	Low Spike (µg/L)	Mid Spike (µg/L)	Compounds	Low Spike (µg/L)	Mid Spike (µg/L)	Compounds	Low Spike (µg/L)	Mid Spike (µg/L)
PFPrA	5	12.5	6:2 FTS	1	2.5	10:2 FTS	1.25	3.125
PFBA	1	2.5	FBSA	1.25	3.125	9Cl-PF3ONS	1	2.5
PFMPA	0.5	1.25	PFPeS	0.25	0.625	PFNS	0.25	0.625
3:3 FTCA	1.25	3.125	PFOA	0.25	0.625	PFDOA	0.25	0.625
PFPeA	0.5	1.25	TFSI	1.25	3.125	PFDS	0.25	0.625
PFPrS	1.25	3.125	7:3 FTCA	6.25	15.625	PFTrDA	0.25	0.625
PFMBA	0.5	1.25	PFHxS	0.25	0.625	11Cl-PF3OUdS	1	2.5
4:2 FTS	1	2.5	PFNA	0.25	0.625	PFOSA	0.25	0.625
PFDHA	0.5	1.25	8:2 FTS	1	2.5	PFTeDA	0.25	0.625
PFHxA	0.25	0.625	NMeFOSAA	0.25	0.625	PFODA	1.25	3.125
PFBS	0.25	0.625	PFHpS	0.25	0.625	PFDOS	0.25	0.625
5:3 FTCA	6.25	15.625	PFDA	0.25	0.625	PFHxDA	1.25	3.125
HFPO-DA	1	2.5	NEtFOSAA	0.25	0.625	NMeFOSE	2.5	6.25
PFEESA	0.5	1.25	PFOS	0.25	0.625	NMeFOSA	0.25	0.625
PFHpA	0.25	0.625	FHxSA	1.25	3.125	NEtFOSE	2.5	6.25
ADONA	1	2.5	PFUnA	0.25	0.625	NEtFOSA	0.25	0.625

3. Results

- A calibration curve ranging from 0.125-2000 µg/L for native PFAS targets with appropriate EIS and NIS concentration was prepared. The RSE values calculated for the calibration curve were less than 15% across all compounds.
- Continuing calibration verification (CCV) was performed after every 10 sample injections as specified by the EPA method 1633A. All accuracies were within 70-130% across all CCVs.

3.1. Soil and Sand Spiked at LLOPR and OPR

- Sample recovery ranged from 38% for PFBSA to 174% for PFOA. PFBSA remains unregulated per EPA 1633A. All 40 compounds, regulated in EPA 1633A met passing criteria for both the LLOPR and OPR spikes, except for PFOA for soil LLOPR. The results for the percent recovery for all compounds are displayed in Figure 4.

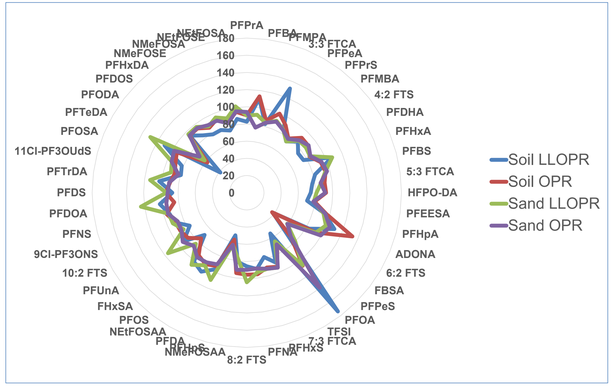

Figure 4. Percent recovery for LLOPR and OPR samples for soil and sand samples.

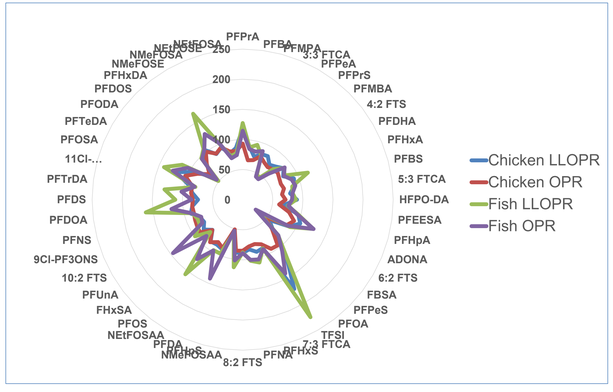

Figure 5. Percent recovery for LLOPR and OPR samples for chicken and fish tissue samples.

3.2. Chicken and Fish Tissue Spiked at LLOPR and OPR

- Sample recovery ranged from 32% for PFBSA to 225% for TFSI. Previously mentioned compound are unregulated by EPA 1633A so there are no clear guideline for the recovery ranges of these compounds.
- 38 compounds regulated in EPA 1633A met passing criteria for both the LLOPR and OPR samples in both chicken and fish tissue. PFPeA and PFHpS fell outside the LLOPR and OPR criteria for EPA 1633A.

4. Conclusions

- The CEM EDGE PFAS automated extraction system, coupled with the Shimadzu LCMS-8065XE, enables robust, high-precision analysis of over 40 PFAS compounds, supporting a streamlined high-throughput workflow while maintaining consistent data quality.

5. Reference

1. Method 1633A Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS.