WP 280

Utilization of Automated Solvent Extraction with a Triple Quadrupole Mass Spectrometer following EPA Method 1633 for PFAS Analysis in Soil

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1. Introduction

- Manual solid sample extraction is error prone and resource consuming, making automation desirable. With the increasing interest in meeting regulatory requirements and understanding PFAS levels in various sample types, automated workflows are essential for improving lab productivity. This work will demonstrate the combined performance of an automated solvent extraction system for soil extraction coupled with a robust LC-MS/MS for PFAS analysis according to EPA Method 1633 to help laboratories with providing accurate results and fast turn-around-times.

2. Methods

- Soil samples comprised of 5 g Ottawa sand were extracted, with the extract being filtered using the CEM EDGE PFAS™ Automated Extraction system with the method detailed below. Samples were weighed into pre-assembled 2-piece Q-Cup® sample cells with Q-Disc® PFAS filter disc and spiked with native PFAS compounds and extracted internal standard. Each sample was then extracted in sequence via the automated addition of solvent via pressurized fluid extraction. Each of the 12 samples was extracted in under 10 minutes, including automated extraction, and automated cleaning of the system (**Figure 1**). Extracts were cleaned-up according to EPA Method 1633 (Millipore-Sigma Carbopack Adsorbent and SupelClean ENVI-WAX SPE Tube) before LCMS analysis.
- The 40 PFAS (targets, non-extracted and extracted internal standards) were chromatographically separated with a C18 column (50x2.1 mm, 3µm) by gradient elution. A C18 delay column was used to remove the interference system PFAS contaminants. The LC and MS parameters used are outlined in **Table 1**.

Table 1. Shimadzu LCMS-8060NX parameters

LC Time Program		Mobile Phase	
Time	**B.Conc**	**A**	2mM ammonium acetate in water
0	2	**B**	Acetonitrile
0.21	20	**Flow Rate**	0.4 mL/min
7	55	**Gas Flow**	
9	98	**Nebulizing**	2 L/min
10.25	98	**Heating**	15 L/min
10.26	2	**Drying**	5 L/min
Injection Volume	15 µL	**Interface Temp.**	250 °C

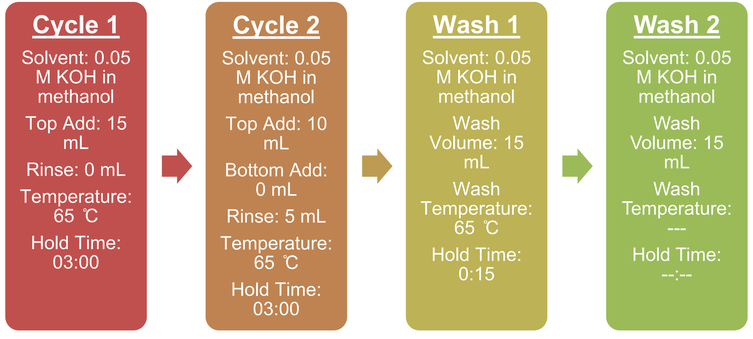
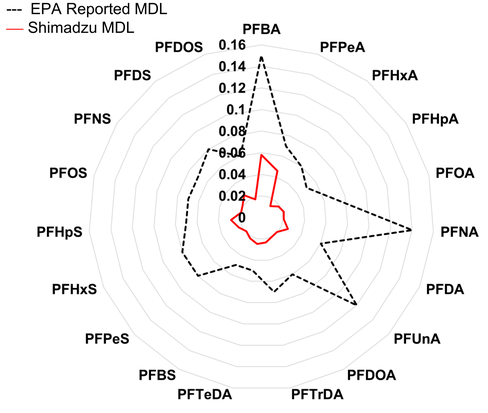


Figure 1. Sample extraction process following EPA 1633 Method with the CEM EDGE PFAS Automated Extraction system

3. Results

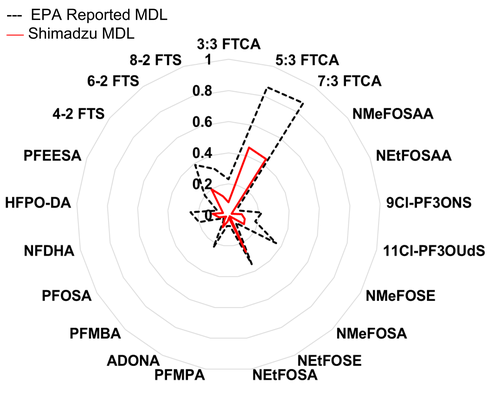
- A calibration curve ranging from 0.02 – 1.25 ng/mL with appropriate Non-Extracted Internal Standard concentrations was prepared. Calibrants were set at concentration starting at 10 times lower than EPA Method 1633 Cal 1 (PFBA: 0.08 ng/mL; variable concentration of targets as listed in EPA 1633[1]) to demonstrate that accurate quantitation of spiked soils can be achieved at limits below the method requirements. The EPA Method 1633 requires an RSE equal to or lower than 20%. The RSE values calculated from the calibration curve were all below 18%.
- Calibration verification was performed after every 10 sample injections as specified by the EPA method; the average %accuracy ranged from 90 – 128% for all targeted PFAS analytes throughout the analysis.
- Sample recovery ranged from 63% (PFDOS) to 115% (PFHxA) and were within the acceptable range listed in EPA Method 1633.
- The method detection limits for spiked samples (MDL_s) were calculated by taking the standard deviation from the concentration of each compound and multiplying it by the appropriate t-value[2]. **Figures 2** and **3** compare the MDLs reported in EPA Method 1633 compared with those from the workflow used in this study combining the EDGE and the LCMS-8060NX, based on the class of PFAS.

References
(1) Method 1633* Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS
(2) Appendix B to Part 136, Title 40 -- Definition and Procedure for the Determination of the Method Detection Limit—Revision 2



EPA Range: 0.05 – 0.15 ng/L; Shimadzu Range: 0.01 – 0.06 ng/L

Figure 2. MDLs comparison between the levels reported in EPA Method1633 and obtained from this work of perfluoroalkyl carboxylic acids and sulfonic acids.



EPA Range: 0.04 – 0.87 ng/L; Shimadzu Range: 0.01 – 0.45 ng/L

Figure 3. MDLs comparison between the levels reported in EPA Method 1633 and obtained from this work of the listed PFAS compounds.

3. Results (Cont.)

- For perfluoroalkyl carboxylic and sulfonic acids (**Figure 2**), MDLs obtained in this work ranged from 0.01 ng/L (PFHxA) to 0.06 ng/L (PFBA). The results from the other classes of PFAS included in EPA Method 1633 are shown in **Figure 3**; results obtained in this work ranged from 0.01 ng/L (NMeFOSA) to 0.45 ng/L (5:3 FTCA).

4. Conclusions

- Overall, the calculated MDLs from this workflow using the CEM EDGE PFAS combined with the Shimadzu LCMS-8060NX were 2 times better than those reported in EPA Method 1633 in soils.
- The combination of the automated solvent extraction system with optimized extraction parameters and the robust sensitive LC-MS/MS demonstrated performance that met the requirements in the final EPA Method 1633.