

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Leachate by EPA Method 1633A Using LC-MS/MS

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1. Overview

A reliable LC/MS/MS method for PFAS in leachate analysis according to EPA M1633A for environmental monitoring and leachate management.

2. Introduction

A recent EPA study found PFAS in over 95% of landfill leachate samples from more than 200 U.S. sites, with concentrations reaching up to 14,000 ppt across 63 different compounds (Figure 1). Despite increasing concern, there are currently no federal regulations for PFAS in landfill leachate, although some states have implemented monitoring and treatment requirements. These findings highlight the

urgent need for national effluent guidelines and pretreatment standards. With PFAS recognized as a persistent global contaminant, regulatory momentum is growing. EPA Method 1633A is currently the only validated multi-lab method for PFAS detection in leachate. Our laboratory has developed a sensitive and reliable LC-MS/MS method to support environmental monitoring and improve leachate management strategies.



Figure 1. Leachate Generation

3. Method

A composite leachate sample from the southern U.S., along with method blanks, two laboratory control samples (LCS), and two spiked leachate samples, was extracted and analyzed following EPA Method 1633A (Figure 2).

Samples were prepared using **solid phase extraction (SPE)** with EVOLUTE® EXPRESS WAX 150 mg/6 mL cartridges. A 100 mL volume was spiked with extracted internal standards (EIS) and passed through the cartridge, then eluted with 1% methanolic ammonium hydroxide, followed by a **carbon cleanup** step. Last, the extracts were spiked non-extracted internal standards (NIS).

Chromatographic separation of 40 PFAS analytes and 31 internal standards was achieved within 14 minutes using a **Shim-pack Scepter C18-120 column** (50 × 2.1 mm, 3 µm) with gradient elution (Figure 3, Table 1).

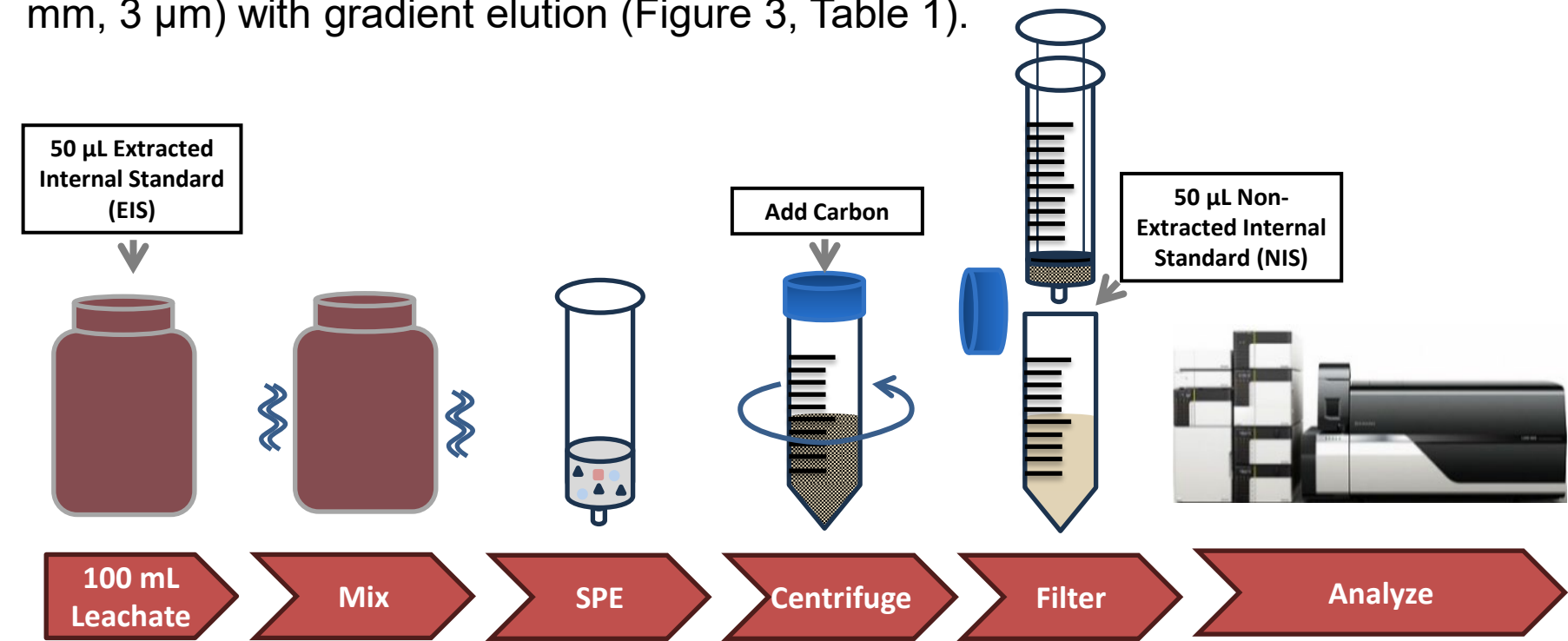


Figure 2. Sample preparation procedure using EPA 1633A for Leachate.

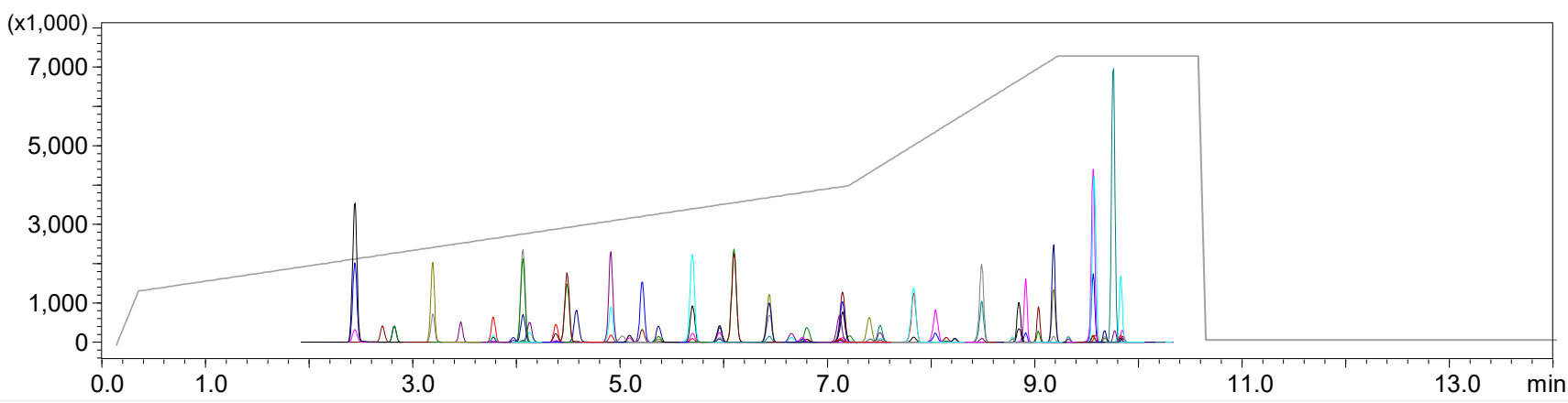


Figure 3. Chromatogram of EPA 1633A method, with %B.

Mobile phases consisted of 2 mM ammonium acetate in water and acetonitrile at a flow rate of 0.4 mL/min. A **Shimadzu Nexcol PFAS Delay column** (50 × 3.0 mm, 5 µm) was used to reduce system-derived PFAS background.

Detection was performed on a Shimadzu LCMS-8060 triple quadrupole mass spectrometer using multiple reaction monitoring (MRM). Calibration ranged from 0.8 to 250 ng/mL for PFBA. LCS and spiked leachate samples were fortified at 10 ng/mL (midpoint) and 1.6 ng/mL (2× low calibrator) PFBA equivalents. Data were acquired and processed using **LabSolutions** and **LabSolutions Insight** software.

Table 1. Compounds in the EPA 1633A method.

| Target Analyte Name | Abbreviation | Target Analyte Name | Abbreviation |
|---|----------------------|--|-----------------|
| Perfluoroalkyl carboxylic acids | | Ether sulfonic acids | |
| Perfluorobutanoic acid | PFBA | 11-Chloroicosasulfuro-3-oxaundecane-1-sulfonic acid | 11Cl-PF30Uds |
| Perfluoropentanoic acid | PFPeA | 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid | 9Cl-PF30NS |
| Perfluorohexanoic acid | PFHxA | Perfluoro(2-ethoxyethane)sulfonic acid | PFEEsA |
| Perfluoroheptanoic acid | PFHpA | Fluorotelomer carboxylic acids | |
| Perfluorooctanoic acid | PFOA | 3:3 Fluorotelomer carboxylic acid | 3:3 FTCA/ FFPa |
| Perfluorononanoic acid | PFNA | 5:3 Fluorotelomer carboxylic acid | 5:3 FTCA/ FPePA |
| Perfluorodecanoic acid | PFDA | 2H,2H,3H,3H-Perfluorodecanoic acid | 7:3 FTCA/ FHPa |
| Perfluoroundecanoic acid | PFUnA | Extracted Internal Standards | |
| Perfluorododecanoic acid | PFDoA/ PFDoDA | Perfluoro-n-[13C4]butanoic acid | 13C4-PFBA |
| Perfluorotridecanoic acid | PFTriDA | Perfluoro-n-[13C5]pentanoic acid | 13C5-PFPeA |
| Perfluorotetradecanoic acid | PFTeDA/ PFTreA/ PFTA | Perfluoro-n-[1,2,3,4,6-13C5]hexanoic acid | 13C5-PFHxA |
| Perfluoroalkyl sulfonic acids | | Perfluoro-n-[1,2,3,4-13C4]heptanoic acid | 13C4-PFHpA |
| Perfluorobutane sulfonic acid | PFBS | Perfluoro-n-[13C8]octanoic acid | 13C8-PFOA |
| Perfluoropentanesulfonic acid | PFPeS | Perfluoro-n-[13C9]nonanoic acid | 13C9-PFNA |
| Perfluorohexanesulfonic acid | PFHxS | Perfluoro-n-[1,2,3,4,5,6-13C6]decanoic acid | 13C6-PFDA |
| Perfluoroheptanesulfonic acid | PFHpS | Perfluoro-n-[1,2,3,4,5,6,7-13C7]undecanoic acid | 13C7-PFUnA |
| Perfluorooctanesulfonic acid | PFOS | Perfluoro-n-[1,2-13C2]dodecanoic acid | 13C2-PFDoA |
| Perfluorononanesulfonic acid | PFNS | Perfluoro-n-[1,2-13C2]tetradecanoic acid | 13C2-PFTeDA |
| Perfluorodecane sulfonic acid | PFDS | Perfluoro-n-[1,2,3,4-13C3]butanesulfonic acid | 13C3-PFBS |
| Perfluorododecane sulfonic acid | PFDS | Perfluoro-n-[1,2,3-13C3]hexanesulfonic acid | 13C3-PFHxS |
| Fluorotelomer sulfonic acids | | Perfluoro-1-[13C8]octanesulfonic acid | 13C8-PFOS |
| 1H,1H,2H,2H-Perfluorohexane sulfonic acid | 4:2FTS | Perfluoro-1-[13C8]octanesulfonamide | 13C8-PFOsA |
| 1H,1H,2H,2H-Perfluorooctane sulfonic acid | 6:2FTS | N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid | D3-NMeFOSA |
| 1H,1H,2H,2H-Perfluorodecane sulfonic acid | 8:2FTS | N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid | D5-NEtFOSA |
| Perfluorooctane sulfonamides | | 1H,1H,2H,2H-Perfluoro-1-[1,2-13C2]hexane sulfonic acid | 13C2-4:2FTS |
| Perfluoro-1-octanesulfonamide | PFOSA/ FOSA | 1H,1H,2H,2H-Perfluoro-1-[1,2-13C2]octane sulfonic acid | 13C2-6:2FTS |
| N-methylperfluorooctanesulfonamide | NMeFOSA/ MeFOSA | 1H,1H,2H,2H-Perfluoro-1-[1,2-13C2]decane sulfonic acid | 13C2-8:2FTS |
| N-ethylperfluorooctanesulfonamide | NEtFOSA/ EtFOSA | Tetrafluoro-2-heptafluoropropoxy-13C3-propanoic acid | 13C3-HFPD-DA |
| Perfluorooctane sulfonamidoacetic acids | | N-methyl-D7-perfluorooctanesulfonamidoethanol | D7-NMeFOSE |
| N-methyl perfluorooctanesulfonamidoacetic acid | NMeFOSA | N-ethyl-D9-perfluorooctanesulfonamidoethanol | D9-NEtFOSE |
| N-ethyl perfluorooctanesulfonamidoacetic acid | NEtFOSA | N-ethyl-D5-perfluoro-1-octanesulfonamide | D5-NEtFOSA |
| Perfluorooctane sulfonamide ethanol | | N-methyl-D3-perfluoro-1-octanesulfonamide | D3-NMeFOSA |
| 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol | N-MeFOSE | Non-Extracted Internal Standards | |
| 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol | N-EtFOSE | Perfluoro-n-[2,3,4-13C3]butanoic acid | 13C3-PFBA |
| Perfluoroalkyl sulfonamide carboxylic acids | | Perfluoro-n-[1,2,3,4-13C4]octanoic acid | 13C4-PFOA |
| Hexafluoropropylene oxide dimer acid | HFPO-DA/ GenX | Perfluoro-n-[1,2-13C2]decanoic acid | 13C2-PFDA |
| 4,8-Dioxo-3H-perfluorononanoic acid | ADONA | Perfluoro-n-[1,2,3,4-13C4]octanesulfonic acid | 13C4-PFOS |
| Perfluoro-3-methoxypropanoic acid | PFMPA | Perfluoro-n-[1,2,3,4,5-13C5]nonanoic acid | 13C5-PFNS |
| Perfluoro-4-methoxybutanoic acid | PFMBA | Perfluoro-n-[1,2,3-13C3]hexanoic acid | 13C3-PFHxA |
| Nonafluoro-3,6-dioxahexanoic acid | NFDHA | | |

4. Results

Figure 4 illustrates the batch structure used to assess method robustness and instrument reliability. The batch began with a triplicate calibration curve to ensure accuracy and reproducibility. After completing the calibration, we performed a continuing calibration check throughout the batch to evaluate consistency and stability throughout the 154-injection sequence, including solvent blanks, standards, controls, and leachate samples over 37 hours of analysis.

All 40 PFAS analytes demonstrated excellent linearity and precision, with relative standard errors (RSE) below 20% using five replicates. CCV recoveries consistently ranged between 70–130%, and concentration variability remained under 15% RSD for all analytes in the panel and under 6% for PFBA represented in Figure 4. This data confirms method and system durability despite numerous complex leachate matrix injections under high-throughput conditions.

Quantifiable PFAS were not detected in the method blank, highlighting the effectiveness of the PFAS delay column and system cleanliness in eliminating background contamination. LCS samples confirmed quantitation accuracy for the extraction process, with all native PFAS recoveries within the 70–130% range, in compliance with EPA Method 1633A criteria.

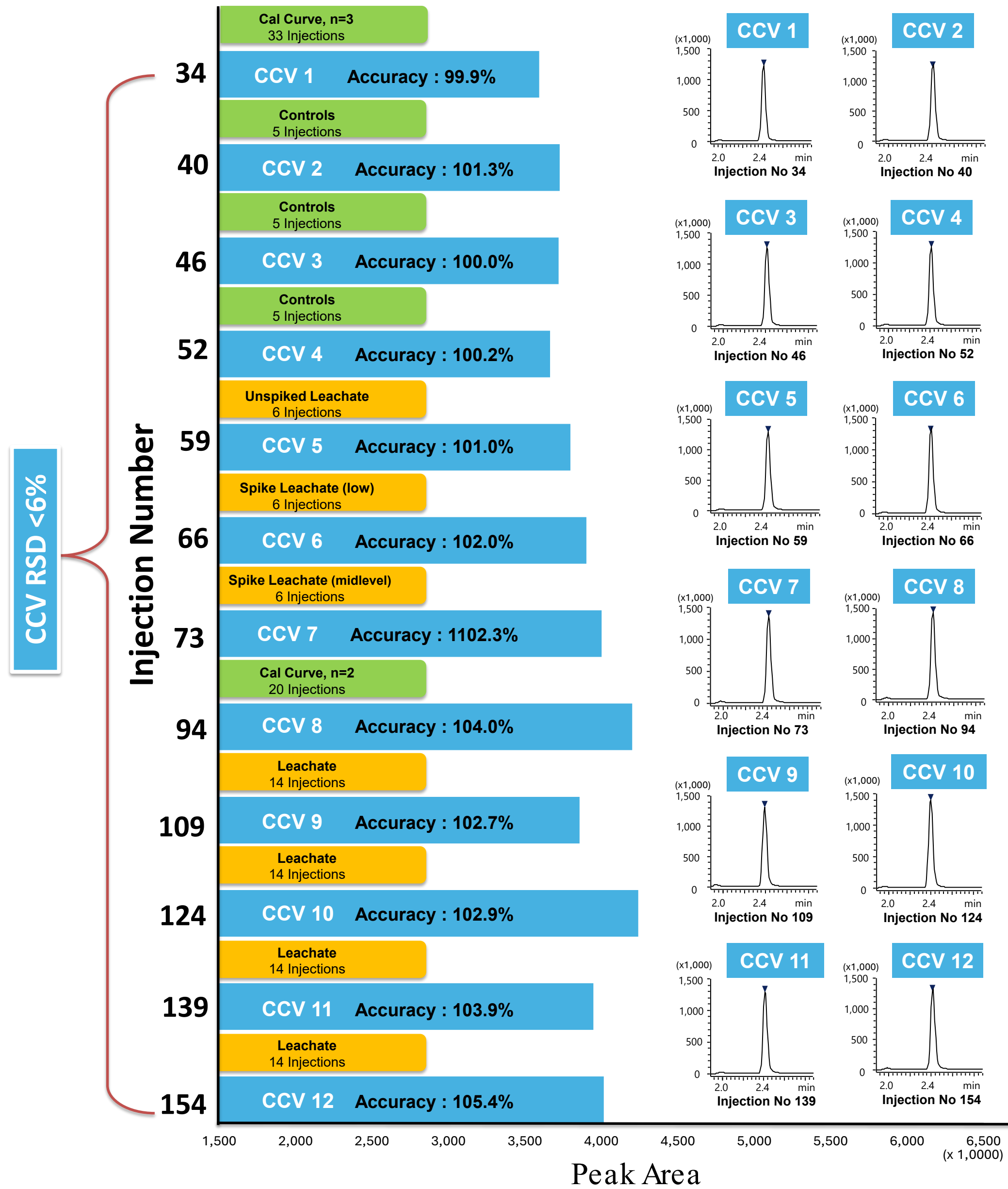


Figure 4. The batch structure designed to assess the performance and reliability. Data for PFAB CCV illustrates reproducibility with a percent RSD less than 6% for PFAB as well as good accuracy and peak shape. The CCV was less than 15% for all analytes included in the panel.

Source saturation was ruled out as a factor for low extracted internal standard (EIS) recovery based on post-extraction dilution experiments. Improved EIS recovery was observed when leachate samples were diluted *prior* to solid phase extraction (Figure 5).

Native PFAS compounds detected in the unspiked, undiluted leachate included: **5:3 FTCA**, **6:2 FTS**, **7:3 FTCA**, **NEtFOSA**, **NMeFOSA**, **PFBA**, **PFBS**, **PFHpA**, **PFHxA**, **PFHxS**, **PFNA**, **PFOA**, **PFOS**, and **PFPeA**.

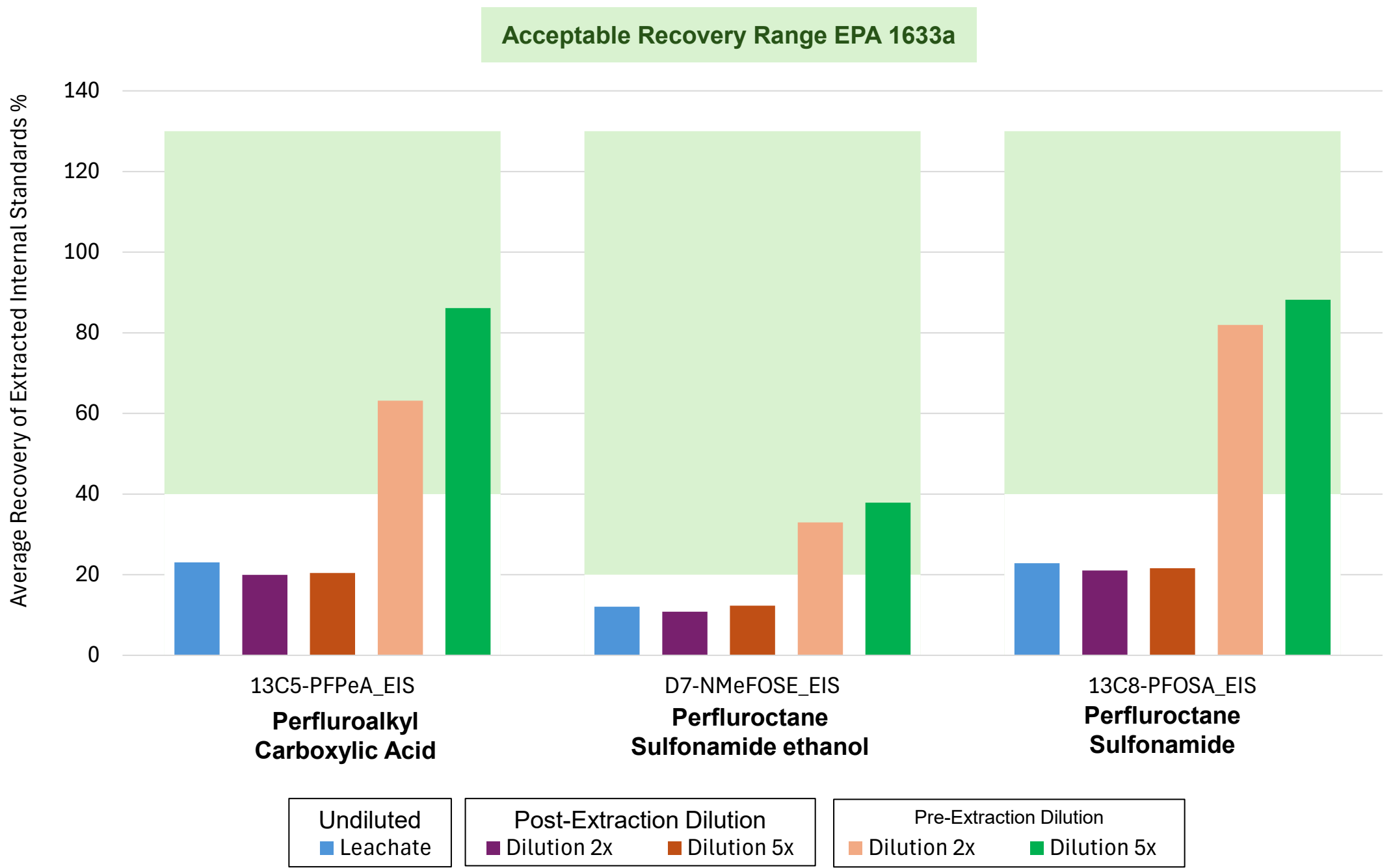


Figure 5. Illustrates the effect of diluting the leachate samples post- and pre-extraction to improve EIS recovery. Leachate samples were diluted 2x and 5x after extraction to evaluate source saturation. In addition, leachate samples were diluted 2x and 5x before extraction to assess the SPE saturation. Undiluted leachate and diluted leachate samples were then compared to the acceptable percent recovery range per EPA 1633a for the extracted internal standard (EIS) in leachate.

5. Conclusion

The Shimadzu LCMS-8060 triple quadrupole system provided robust, stable performance over 154 injections and 37 hours of continuous PFAS analysis. With effective background reduction and rapid separation, the method follows EPA 1633A and is ideal for routine monitoring of complex leachate matrices.

6. Reference

- U.S. Environmental Protection Agency. **Effluent Guidelines Program Plan 15**. January 2023. *Landfills Effluent Guidelines*. Available at: <https://www.epa.gov/eg/landfills-effluent-guidelines>
- U.S. Environmental Protection Agency. **Method 1633, Revision A**. December 2024. *Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS*. Available at: <https://www.epa.gov/system/files/documents/2024-12/method-1633a-december-5-2024-508-compliant.pdf>

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