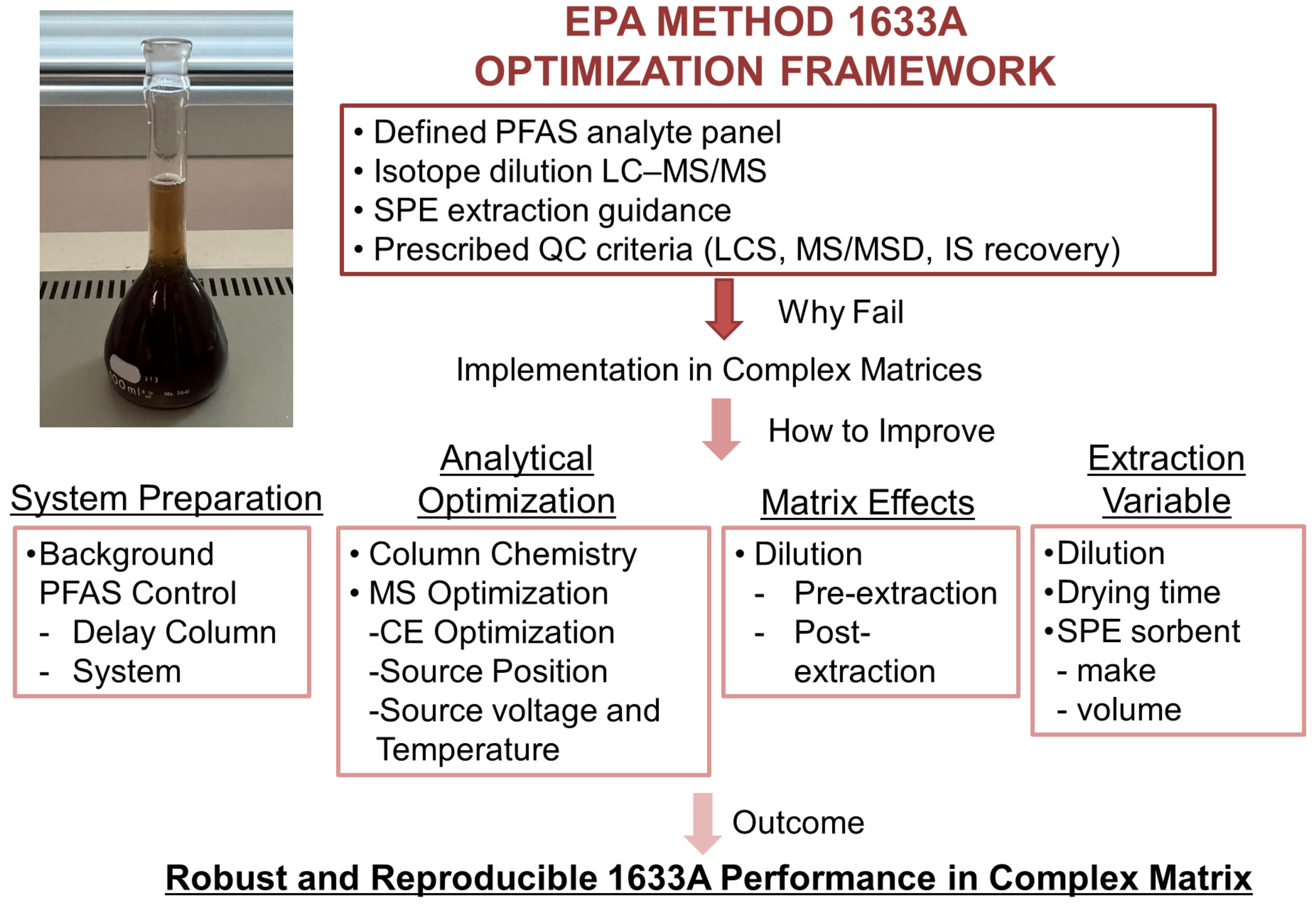
SHIMADZU

WP 255

PFAS Analysis of Leachate: Evaluating Key Sample Preparation and LC–MS/MS Parameters for Improved Performance

Tiffany Liden[1], Kate (Xiaomeng) Xia[1], Vikki Johnson[1], Om Shrestha[1], Ruth Marfil-Vega[1], Kevin Schug[2], Evelyn Wang[1]
(1) Shimadzu Scientific Instruments, Columbia MD; (2) University of Texas at Arlington, Arlington, TX

Introduction: Landfill leachate is a highly complex and variable matrix that poses significant challenges for the analysis of per- and polyfluoroalkyl substances (PFAS). Although U.S. Environmental Protection Agency Method 1633A provides a standardized framework for PFAS quantitation,[1] analytical performance remains strongly influenced by sample preparation, chromatographic separation, and mass spectrometric conditions. Landfill leachate samples were extracted using WAX SPE following EPA 1633A and analyzed by LC–MS/MS using a Shimadzu LCMS-8060 under negative ESI conditions. This study **evaluates the key factors governing LC–MS/MS sensitivity, signal response, and reproducibility in landfill leachate,** including a systematic assessment of SPE, chromatographic behavior, and ion-source conditions across PFAS classes (Figure 1).



EPA METHOD 1633A OPTIMIZATION FRAMEWORK

- Defined PFAS analyte panel
- Isotope dilution LC–MS/MS
- SPE extraction guidance
- Prescribed QC criteria (LCS, MS/MSD, IS recovery)

Why Fail

Implementation in Complex Matrices

How to Improve

System Preparation
- Background PFAS Control
  - Delay Column
  - System

Analytical Optimization
- Column Chemistry
- MS Optimization
  - -CE Optimization
  - -Source Position
  - -Source voltage and Temperature

Matrix Effects
- Dilution
  - Pre-extraction
  - Post-extraction

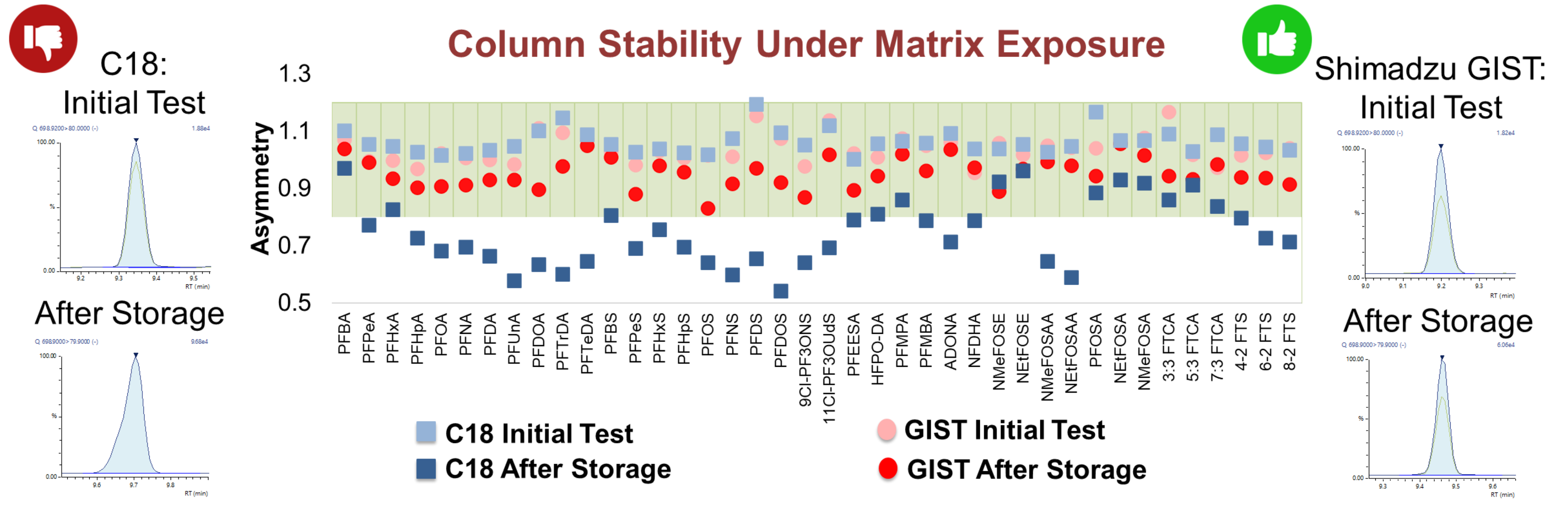
Extraction Variable
- Dilution
- Drying time
- SPE sorbent
  - make
  - volume

Outcome

Robust and Reproducible 1633A Performance in Complex Matrix

Figure 1. Landfill leachate (Top Left) and Optimization process (Right)

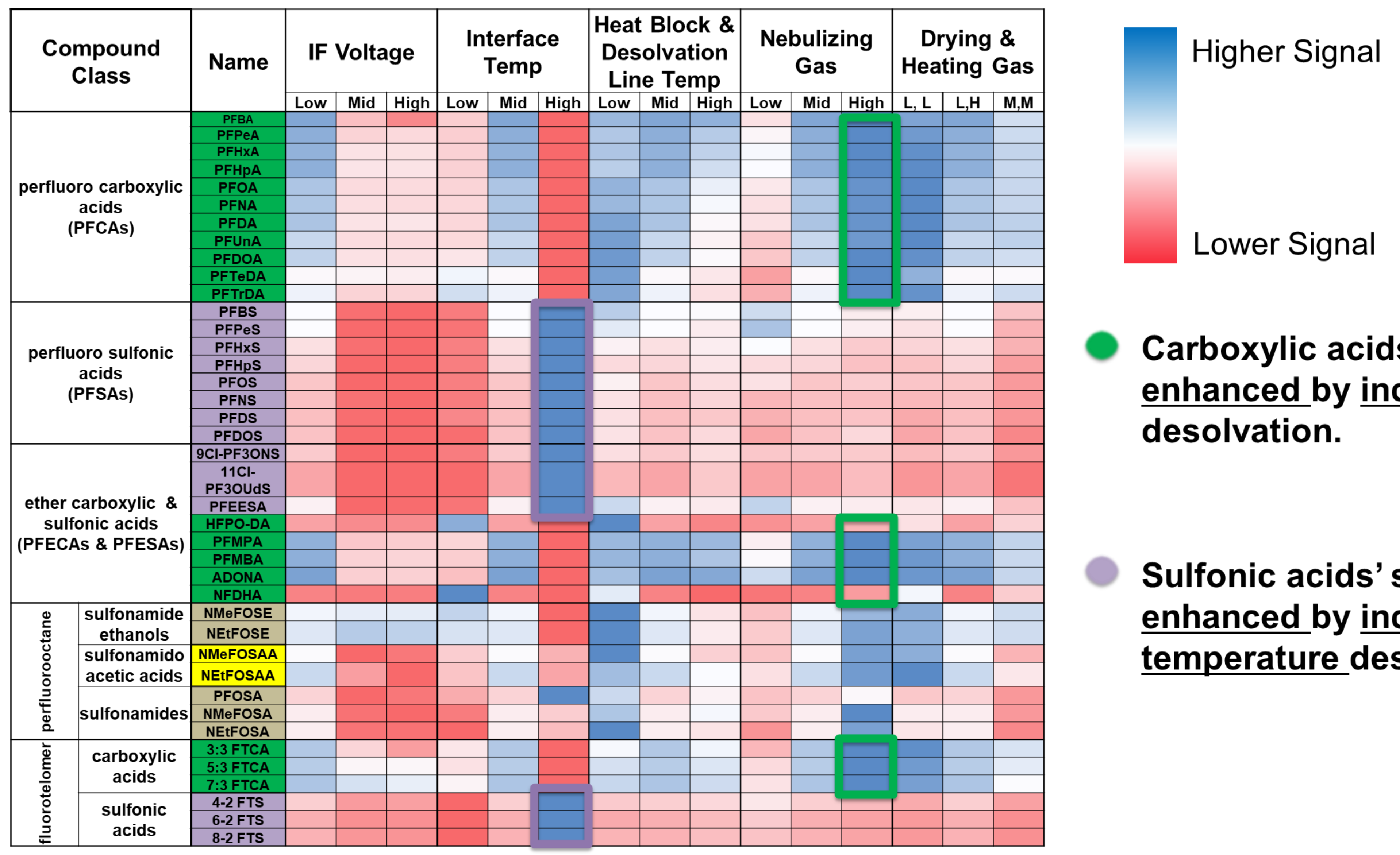
Results: Chromatographic performance was evaluated across four C18 columns (A–D) using peak area, height, asymmetry, and HETP. Two columns produced a higher signal and improved peak shape, while the remaining columns showed greater efficiency. Under repeated batches followed by storage in acetonitrile, **the Shimadzu GIST column produced a consistent signal (≤15% change), whereas another column showed 20–50% signal loss,** particularly for long-chain PFAS and precursors, indicating greater susceptibility to matrix accumulation (Figure 2).



Column Stability Under Matrix Exposure

Figure 2. Graph of asymmetry of a new column (GIST and alternate C18) with standards vs after storage in acetonitrile and reevaluated. The standard acceptable asymmetry range is 0.8 to 1.2, shown in green. Peaks for PFDoS are shown to the left and right for an alternate C18 column and GIST, respectively.

Ion source effects were class-dependent and driven by aerosol and thermal desolvation. Short-chain PFCAs were more sensitive to nebulizing and drying gas, indicating aerosol-driven response, while PFSAs showed greater gains with increased temperature, consistent with thermal desolvation. Increasing the interface voltage reduced the signal, suggesting fragmentation. **Overall, PFCAs favored aerosol processes, whereas PFSAs favored thermal desolvation (Figure 3).**

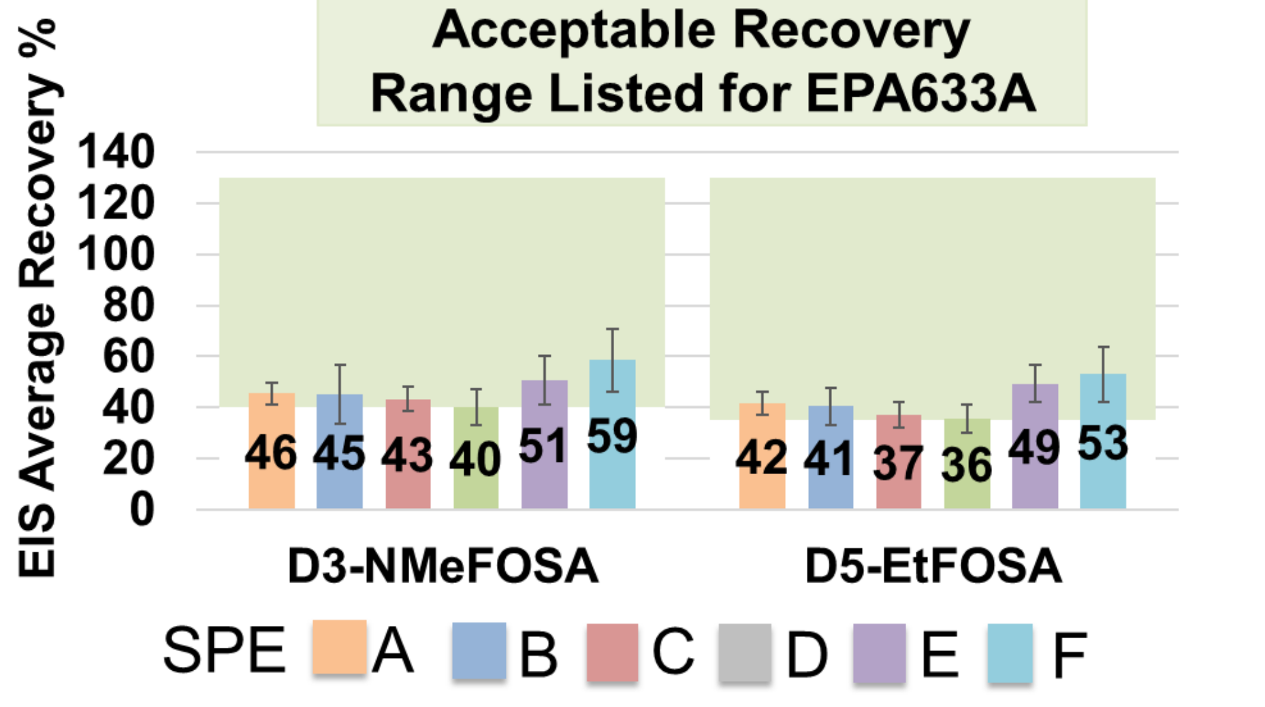


Compound-Class Ionization Behavior

- **Carboxylic acids' signal is <u>enhanced</u> by <u>increased gas desolvation</u>.**
- **Sulfonic acids' signal is <u>enhanced</u> by <u>increased temperature</u> desolvation.**

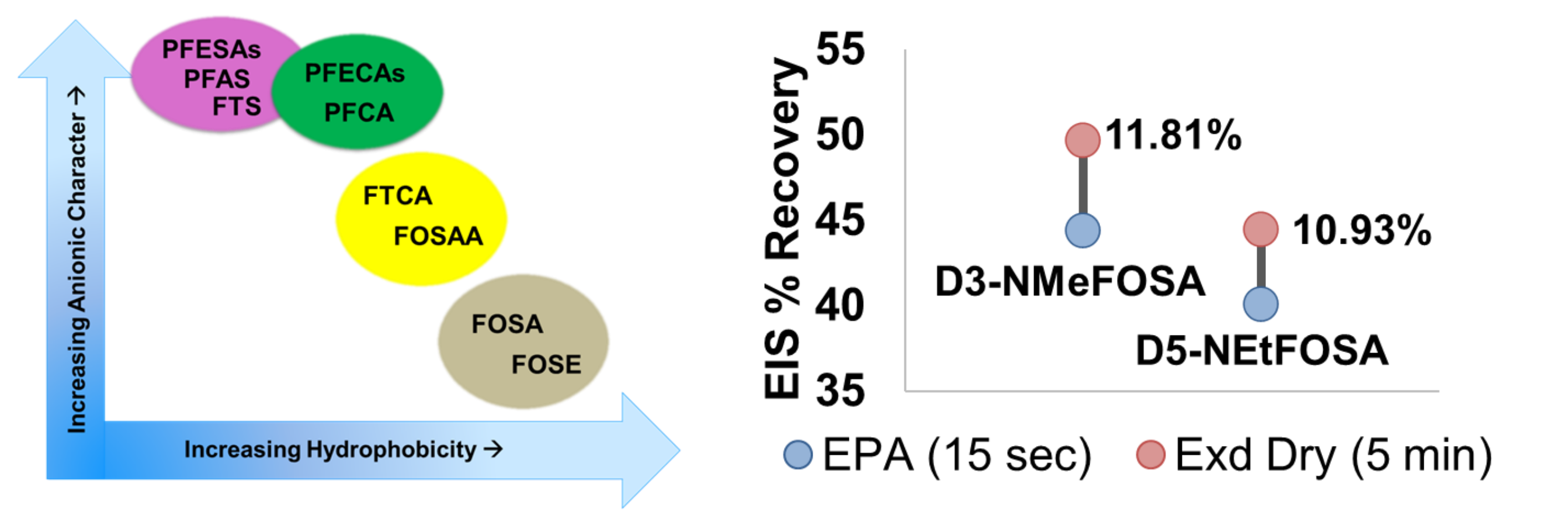
Figure 3. Heat map representing the areas from source optimization tests for each EPA 1633A analyte.

Due to poor recoveries of neutral PFAS, six commercially available SPE cartridges (A–F) were evaluated following the EPA 1633A protocol. D3-NMeFOSA and D5-EtFOSA were the most challenging analytes, exhibiting average recoveries of ~40–59% and ~36–53%, respectively, indicating a mismatch between WAX chemistry and more hydrophobic, less ionic analytes that are only weakly retained on WAX sorbents. **Only sorbents E and F (Millipore Sigma 200 mg and 500 mg bed volume) consistently fell within the target ranges for both compounds.** (Figure 4).



Class-Dependent SPE Retention Behavior

Figure 4. EIS recovery of D3NMe- and D5NEtFOSA using 6 commercially available WAX following EPA guidelines.

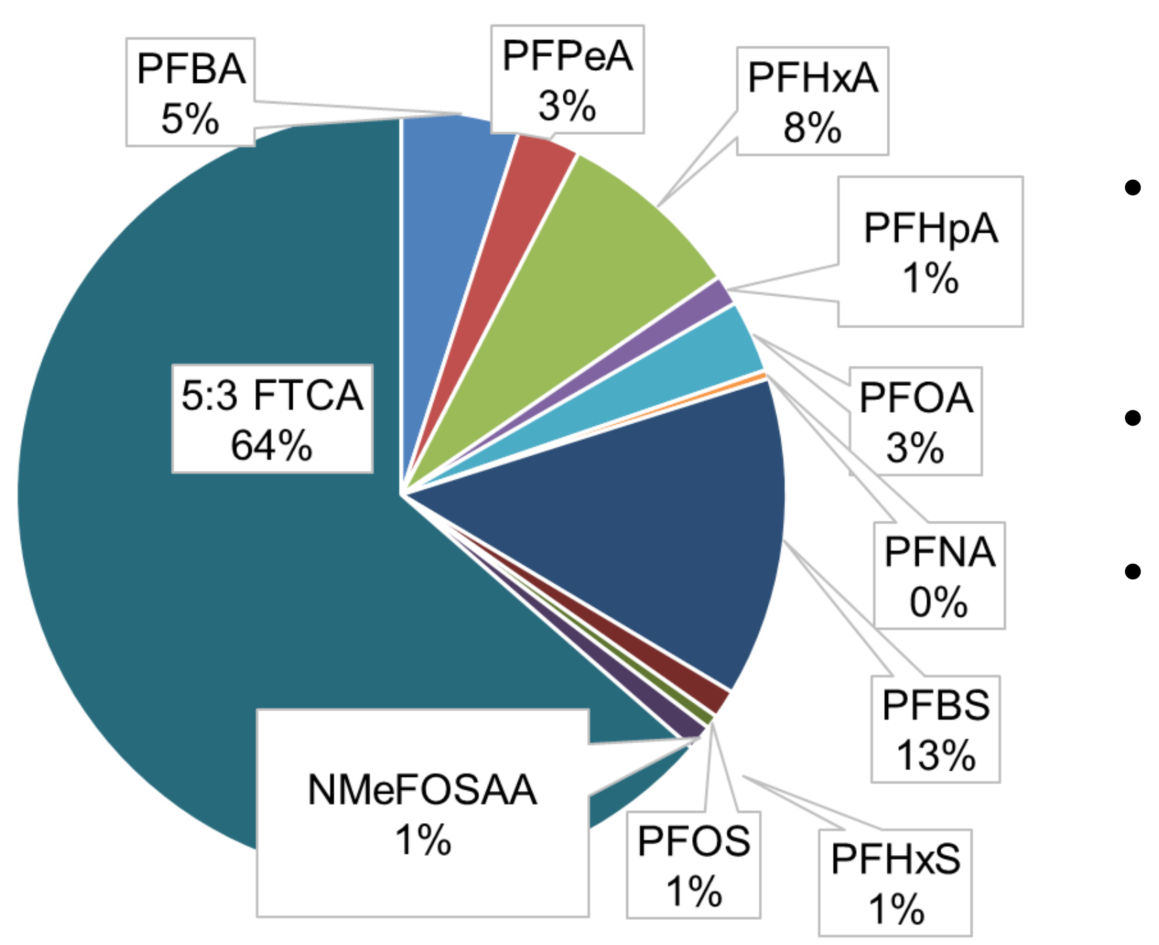


PFAS Behavior Map for WAX SPE Retention

Increased % Recovery with Increased SPE Drying Time

Figure 5. (Left) PFAS Behavior Map for WAX SPE Retention. (Right) Increased SPE drying time.

Because neutral PFAS rely more heavily on hydrophobic interactions, sufficient drying is critical to remove residual water from the sorbent bed. Residual water can reduce analyte retention and limit elution efficiency by disrupting analyte–sorbent interactions and solvent penetration during extraction.[2] By optimizing the EPA **1633A drying conditions, the neutral PFAS analytes evaluated in this study demonstrated a ~12% increase in recovery** beyond sorbent selection. (Figure 5) The most abundant fluorinated compound detected in landfill leachate was 5:3 FTCA (239 ng/mL), commonly seen due to its use in carpet applications (Figure 6).[3]



Total PFAS 376 ng/mL

Figure 6. Graphical representation of the native PFAS in landfill leachate from the southern part of the U.S.

Conclusion:

- PFAS analytical performance was dependent on compound-class-dependent extraction, chromatography, and ionization behavior.
- GIST demonstrated lower signal variability under repeated matrix exposure, with lower signal degradation than alternative C18 phases.
- Neutral PFAS showed poor retention on WAX sorbents, requiring optimization beyond standard EPA 1633A extraction conditions.
- PFCA response was more influenced by gas flow conditions, whereas PFSA response was more sensitive to source temperature conditions.

References:

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*; EPA 821-R-24-005; Washington, DC, 2024.
2. Douglas E. Raynie and Dawn Wallace Watson, "Understanding and Improving Solid-Phase Extraction," *LCGC North America* **32**(12), 2014.
3. Omaojo, U.; Quinete, N. PFAS in Municipal Landfill Leachate: Occurrence, Transformation, and Sources. *Science of the Total Environment* **2024**, *908*, 168197.