Validation of Analysis of Per- and Polyfluoroalkyl Substances in Wastewater Samples Using EPA Method 1633 with a Vacuum-based Automated Solid Phase Extraction System

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Introduction

Per- and polyfluoroalkyl substances (PFAS) constitute a group of compounds characterized by perfluorinated or polyfluorinated carbon chain moieties, typically denoted by structures such as F(CF2)n or F(CF2)n-(C2H4)n. Due to their unique properties, these substances have found extensive application in various industrial and consumer products.

Many industrial and consumer applications utilize perfluorooctane sulfonate (PFOS) and other PFAS compounds. These include but are not limited to, stain-resistant coatings for textiles, leather, and carpets; grease-proof coatings for food-contact paper products; firefighting foams; surfactants for mining and oil-well operations; floor polishes; and insecticide formulations. Their widespread usage has led to their ubiquitous presence in the environment.

In recent years, mounting concerns have emerged regarding the widespread distribution and potential adverse effects of PFAS, particularly notable compounds like PFOS and perfluorooctanoic acid (PFOA). These concerns have prompted intensified scrutiny of the environmental occurrence, fate, and potential impacts of these substances.

Recent developments in the United States have led to the introduction of EPA method 1633, which addresses the need for robust methodologies to monitor and analyze PFAS. This method, unveiled in early 2024, enables comprehensive analysis across various matrices, including wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. EPA Method 1633 represents a significant advancement in the analytical toolkit for assessing PFAS contamination and understanding their distribution and behavior in diverse environmental compartments.

Instrumentation

- FMS TurboTrace PFC™ System. The system is modular in nature and can be extended to a total of four modules, allowing for a maximum of eight samples to be processed in parallel.
- Vacuum pump
- Agilent 6475 TripleQuad LC/MS

Consumables

- FMS Inc. PFAS 50mg GBC/WAX 250 mg cartridges
- Ultrapure DI water
- Methanol pesticide grade
- Ammonium hydroxide
- Formic acid
- Relevant PFAS spiking standards

Method

- Eight synthetic wastewater samples (500 mL) spiked with native PFAS standards and relevant internals
- Load sample bottles onto system and install cartridges
- Rinse bottles are automatically filled during procedure
- Use positive pressure (nitrogen) for pumping solvents and mixes through the system and use vacuum to load the samples
- Condition cartridges with 15 mL 1% methanolic ammonium hydroxide followed by 5 mL of 0.3M formic acid.
- Load samples across the cartridges at 5-10 mL/min (vacuum ~ 8-inch Hg)
- Sample bottles rinsed with 5 mL reagent water (twice) followed by 5 mL of 1:1 0.1M formic acid/methanol and load rinses across the cartridges
- Dry 15 seconds
- Rinse sample bottles with 5 mL 1% methanolic ammonium hydroxide
- Load rinses across cartridges and collect in polypropylene tubes
- Cleanup over 10 mg of loose carbon
- As per the method no further concentration is carried out.

Further relevant standards were added prior to LC/MS analysis

Results

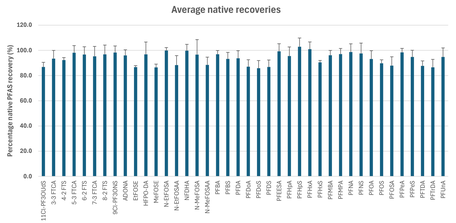

Figure 1. Recoveries of native PFAS compounds in method 1633 synthetic wastewater extracts at 1-38 ng/L.

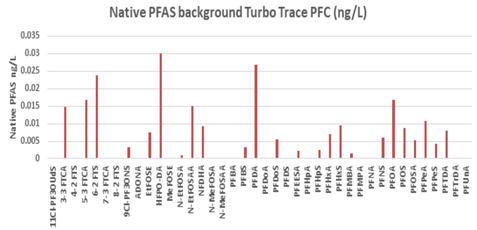

Figure 2. Native background of various PFAS using the automated SPE system.

Discussion and Conclusions

40 native PFAS compounds in synthetic wastewater were analyzed using EPA method 1633 (Figure 1) with the Turbo Trace PFC. All native spike recoveries were within the acceptance windows of the method with RSDs (%) all < 12%. Run time of the automated system is 70 min. Note that with method 1633 no final concentration step is required. The Turbo Trace PFC produces very good recoveries with low standard deviations.

Note that the system has low, partially non-detect, native background values for PFAS and that the risk of cross-contamination is low (Figure 2). Values are < 0.03 ng/L.
The Turbo Trace PFC system produces excellent data for complex sample matrices associated with wastewater, biosolids, and solids, as required by EPA Method 1633.

The system is easy to operate and has unique dual pump capability of positive pressure and vacuum, allowing it to run drinking water or wastewater samples directly from the sample to the cartridge, reducing the chance of breakdown and contamination. Cleaning the system between runs is a quick and easy process. A problem with ground and wastewater extraction is the presence of particulate matter, which can easily clog cartridges, damage syringe-based systems, and block valves, resulting in costly repairs. The use of inline sample bottle filters and the plastic filtration wool in the barrel of the cartridges can eliminate this problem. In this work, no clogging of cartridges occurred. The Turbo Trace PFC system is a high-throughput Automated SPE system for complex matrices for the analysis of PFAS.

For additional information, please contact:

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Automated Turbo PFC system