

Introduction

Per- and Polyfluoroalkyl Substances (PFAS) encompass compounds containing perfluorinated or polyfluorinated carbon chain moieties, such as F(CF2)n- or F(CF2)n-(C2H4)n. Over recent years, heightened concerns have arisen regarding the presence and levels of these chemicals, including PFOS (perfluoro sulfonate) and PFOA (perfluoro-octanoic acid), in the global environment due to their persistence and potential adverse effects. Consequently, PFAS has become subject to increasing regulatory scrutiny in many countries.

The Environmental Protection Agency (US EPA) has issued various methods for extracting and analyzing PFAS compounds, including EPA methods 533, 537.1, and 1633. Solid Phase Extraction (SPE) has emerged as a widely accepted technique for such analyses. This study describes a semi-automated system designed explicitly for PFAS extraction, which proves particularly effective in reducing background contamination. The extraction process for aqueous samples typically takes around 60 minutes.

The application discussed here is about wastewater analysis, aligning with the recently finalized method 1633 prescribed by the US EPA. This method is crucial for accurately assessing PFAS levels in wastewater samples, facilitating effective monitoring and regulatory compliance efforts.

Materials and methods Instrumentation

- FMS, Inc. EZPFC[®] PFAS SPE system (Solid Phase Extraction) is a semi-automated system designed for handling aqueous samples. The system can accommodate up to twelve samples. It has two Stages: Stage 1 for conditioning and sample loading to waste and Stage 2 for collection. It uses a vacuum pump to carry out the various steps.
- Vacuum pump
- Agilent 6475 TripleQuad LC/MS

Consumables

- FMS PFAS WAX 150 mg cartridges
- Ultrapure DI water
- Methanol pesticide grade
- Ammonium hydroxide
- Formic acid
- Relevant PFAS spiking standards



EZPFC



Analysis of Per- and Polyfluoroalkyl Substances in Wastewater Using EPA Method 1633 with Semi-Automated Solid Phase Extraction

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Method EZPFC

- Twelve synthetic wastewater samples (500 mL) spiked with native PFAS standards and relevant internals
- Load sample bottles onto system and install cartridges
- Fill rinse bottles with 5 mL reagent water
- Turn on vacuum (stays on rest of procedure)

Stage 1

- 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 (~ 8-inch Hg)
- Sample bottles rinsed with 5 mL reagent water (twice), followed by 5 mL of 1:1 0.1M formic acid/methanol (using nitrogen)
- Rinses loaded across cartridges • Dry 15 sec under vacuum

Stage 2

- Rinse sample bottles with 5 mL 1% methanolic ammonium hydroxide
- Load rinses across cartridges and collect in polypropylene tubes
- As per the method no further concentration is carried out.
- Further relevant standards were added prior to LC/MS analysis.

Analysis

- Take aliquot from final 5 mL extract
- Analyze with LC/MS



Figure 1. Demonstration of Capability for 40 native PFAS compounds. (Recoveries of native PFAS).

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Results

MDL data 1633 for native PFAS on EZPFC



PFD0/2 PF



Figure 3. Native PFAS in tap, river, and well water



Discussion & Conclusions

In this study, EPA Method 1633 was employed with the EZPFC to analyze 40 native PFAS compounds. Validation procedures included demonstrating capability, wherein four synthetic wastewater samples spiked with native compounds ranging from 4 to 100 ng/L were analyzed to determine average recoveries with associated Relative Standard Deviations (RSDs). Method Detection Limits (MDLs) were established by running seven replicates on the system spiked with concentrations ranging from 0.3 to 6 ng/L.

The validation results indicated robust performance, with MDLs ranging from 0.05 to 1.1 ng/L, underscoring the sensitivity and reliability of the analytical method. Tap, river, and well water samples were analyzed, revealing consistent trends in native PFAS concentrations across all matrices assessed (Figure 3).

Furthermore, the background contribution from the EZPFC system was exceedingly low, with levels below 0.02 ng/L (Figure 4). This minimal background contamination is attributed to the system's design, which incorporates stainless-steel surfaces and polypropylene tubing to facilitate sample extraction with minimal native contamination.

Comparison between the Semi-Automated and automated SPE systems demonstrated comparable performance, affirming the efficacy and ease of operation of the EZPFC system. Notably, the system's design, featuring only a vacuum pump as a mechanical component, ensures straightforward operation and expedited cleaning between runs.

A notable challenge in ground- and wastewater extraction is the presence of particulate matter, which can potentially lead to cartridge clogging. However, using plastic filtration wool within the cartridge barrel mitigated this issue, as evidenced by the absence of observed cartridge clogging in this study.

Overall, the results demonstrate the suitability of the EZPFC system for PFAS analysis, offering high sensitivity, minimal background contamination, ease of operation, and robust performance across various water matrices. These findings underscore the system's potential for widespread adoption in environmental monitoring and regulatory compliance initiatives.



Figure 4. Native PFAS background contribution.

For additional information please contact:

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