

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

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Introduction

Per- and Polyfluoroalkyl Substances (PFAS) contain a perfluorinated or polyfluorinated carbon chain moiety such as F(CF₂)_n- or F(CF₂)_n-(C₂H₄)_n. In recent years there has been increasing concern over the levels of these chemicals, (e.g., PFOS (perfluoro sulfonate), and PFOA (perfluoro-octanoic acid)) in the global environment because of their fate and possible adverse effects. PFAS are subject to varying but increasing levels of control in many countries.

In the United States the Environmental Protection Agency (US EPA) has released various methods for extraction and analysis of PFAS compounds such as 533, 537.1 and 1633 (draft). Solid Phase Extraction (SPE) has become a well-accepted technique for these kinds of analyses. In this study we describe both a fully automated and a semi-automated system that was made specifically for PFAS extraction. Primarily effective at reducing background contamination, extraction of aqueous samples takes about 70 min. The application described here is for wastewater analysis following draft method 1633.

Materials and methods

Instrumentation

- FMS, Inc. TurboTrace® Parallel/Sequential PFAS SPE system (Solid Phase Extraction) is a modular expandable system designed for handling wastewater samples. The system can have from one to six modules. Each module can run 5 samples sequentially, the system can be expanded from one to 6 modules to run a total of 5 to 30 samples.
- FMS EZPFC® System
- Vacuum pump
- Agilent 6475 TripleQuad LC/MS

Consumables

- Agilent Bond Elut PFAS WAX 250 mg cartridges
- Ultrapure DI water
- Methanol pesticide grade
- Ammonium hydroxide
- Formic acid
- Relevant PFAS spiking standards

Method Parallel/Sequential

- Six synthetic wastewater samples (500 mL) spiked with 50 ppt 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 (~ 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 sec
- 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.

Method EZPFC

- Twelve synthetic wastewater samples (500 mL) spiked with 50 ppt 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

Results

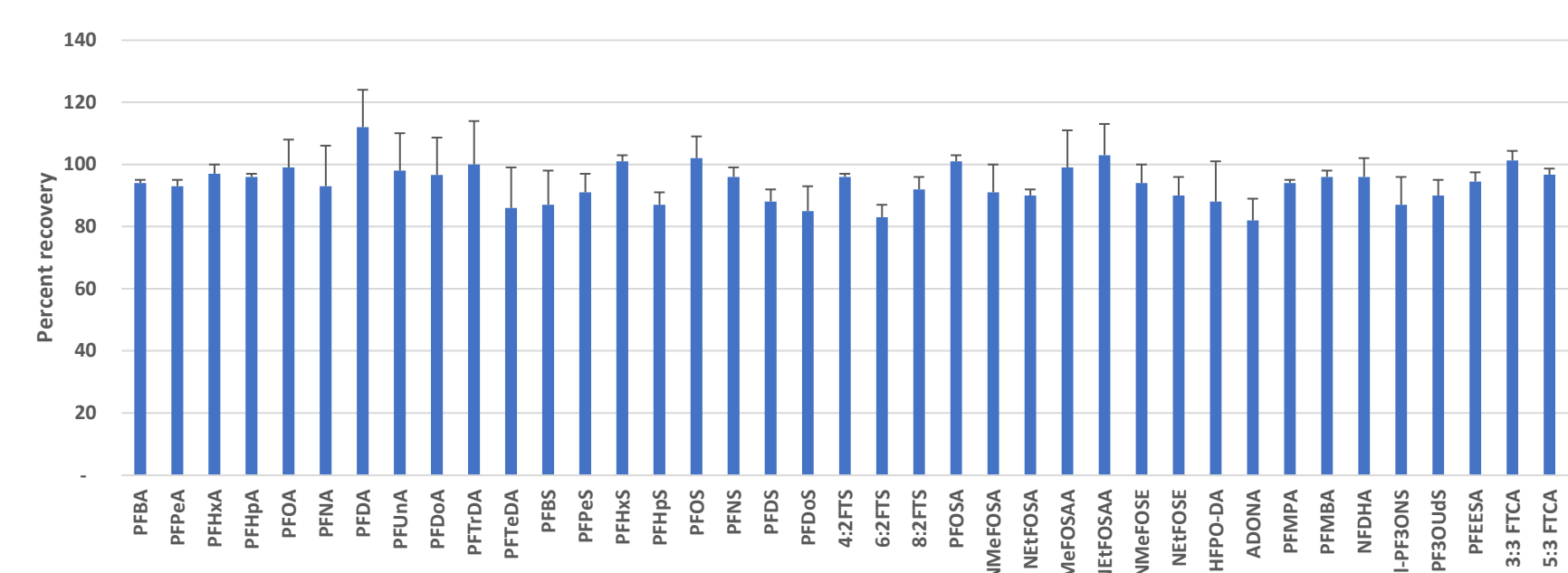


Figure 1. Recoveries of 40 native PFAS using the automated parallel/sequential SPE system.

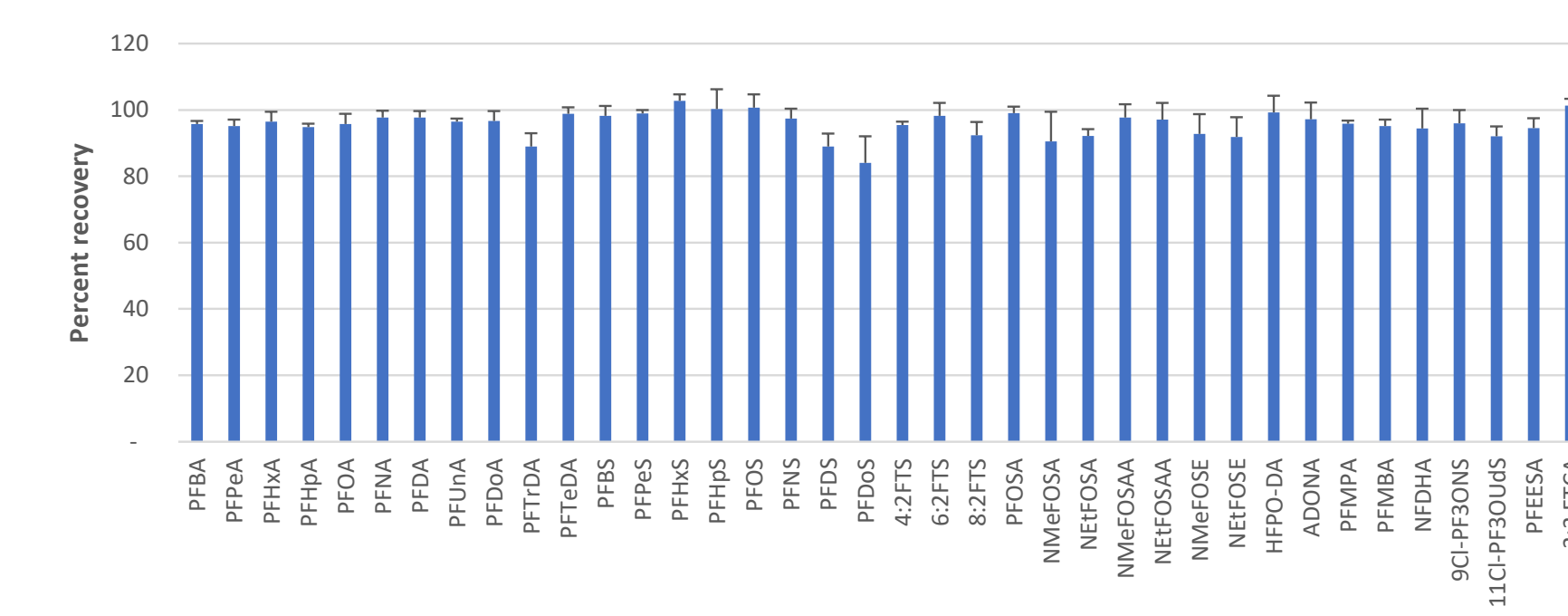


Figure 2. Recoveries of 40 native PFAS using the EZPFC semi-automated system.

Conclusions

A total of 40 native PFAS compounds were analyzed using EPA method 1633 with the parallel/sequential system.(Figure 1). All recoveries were 75% or higher with RSDs (%) all < 15%. All PFAS recoveries were within the acceptance windows (different for each compound) required by the method. Total run time of the automated system is < 70 min. The automated system produces very good recoveries with low standard deviations.

The semi-automated SPE system produces data that is as good as the automated SPE system (Figure 2).The system is easy to operate and has only the vacuum pump as a mechanical part. Cleaning the system between runs is very quick and easy.

The background contribution from the parallel/sequential system is very low (< 0.05 ng/L, Figure 3). The design of the system, with stainless-steel surfaces and polypropylene tubing, ensures sample extraction with very low native background contamination.

An important problem with ground- and wastewater extraction is the presence of particulate matter which can easily plug up cartridges. Use of plastic filtration wool in the barrel of the cartridges can eliminate this problem. In this work no clogging of cartridges was observed.

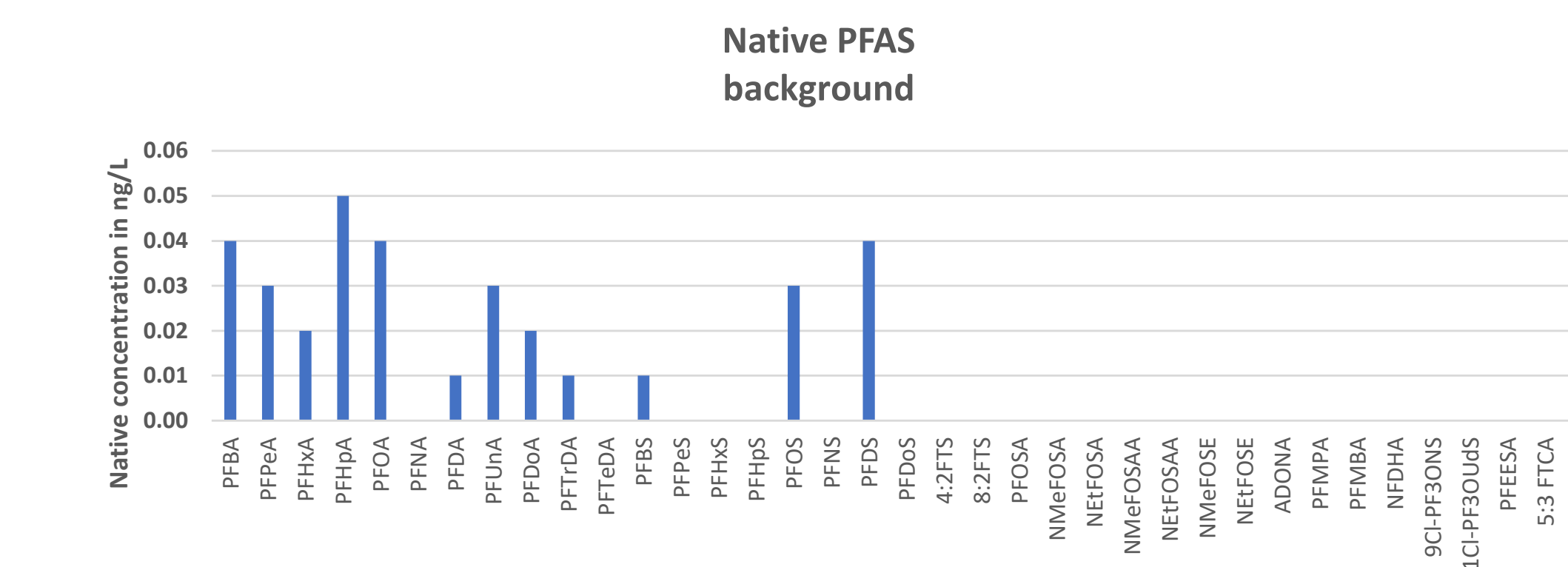
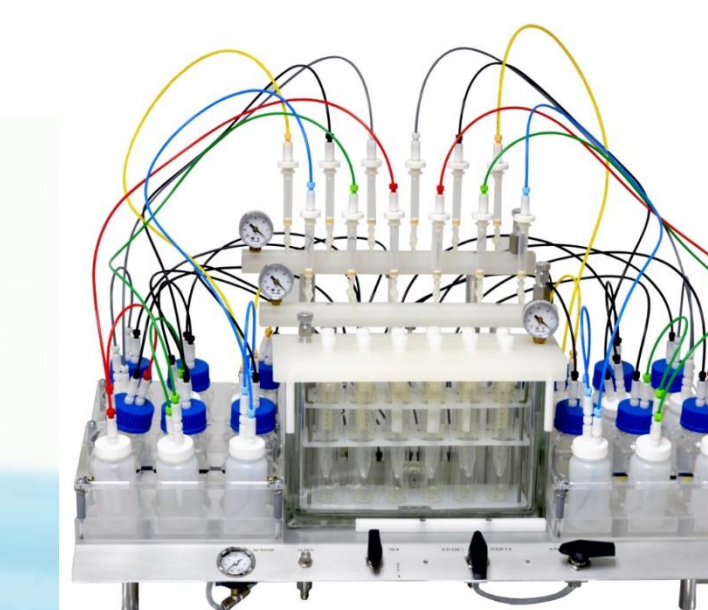


Figure 3. Native PFAS background contribution.

Parallel/Sequential System



EZPFC



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Sample Extraction

Sample Clean Up

Sample Concentration