

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 $F(CF_2)_n-$ or $F(CF_2)_n-(C_2H_4)_n$. 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

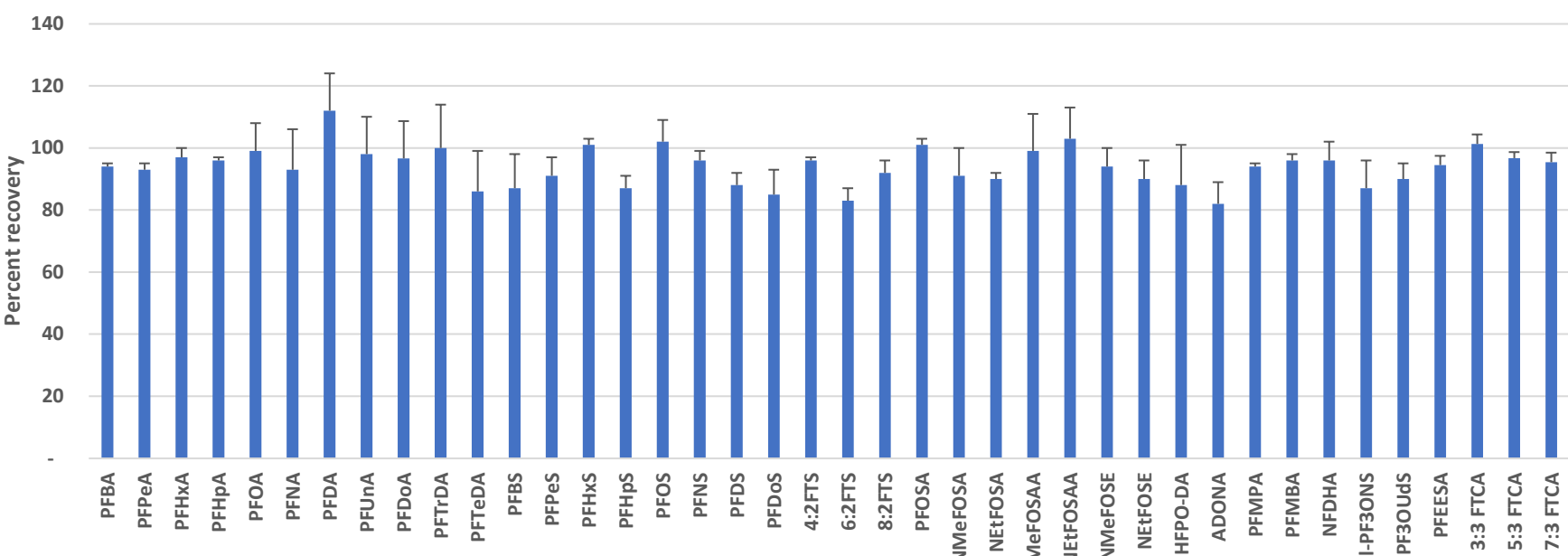


Figure 1. Recoveries of 40 native PFAS using the automated parallel/sequential SPE system.

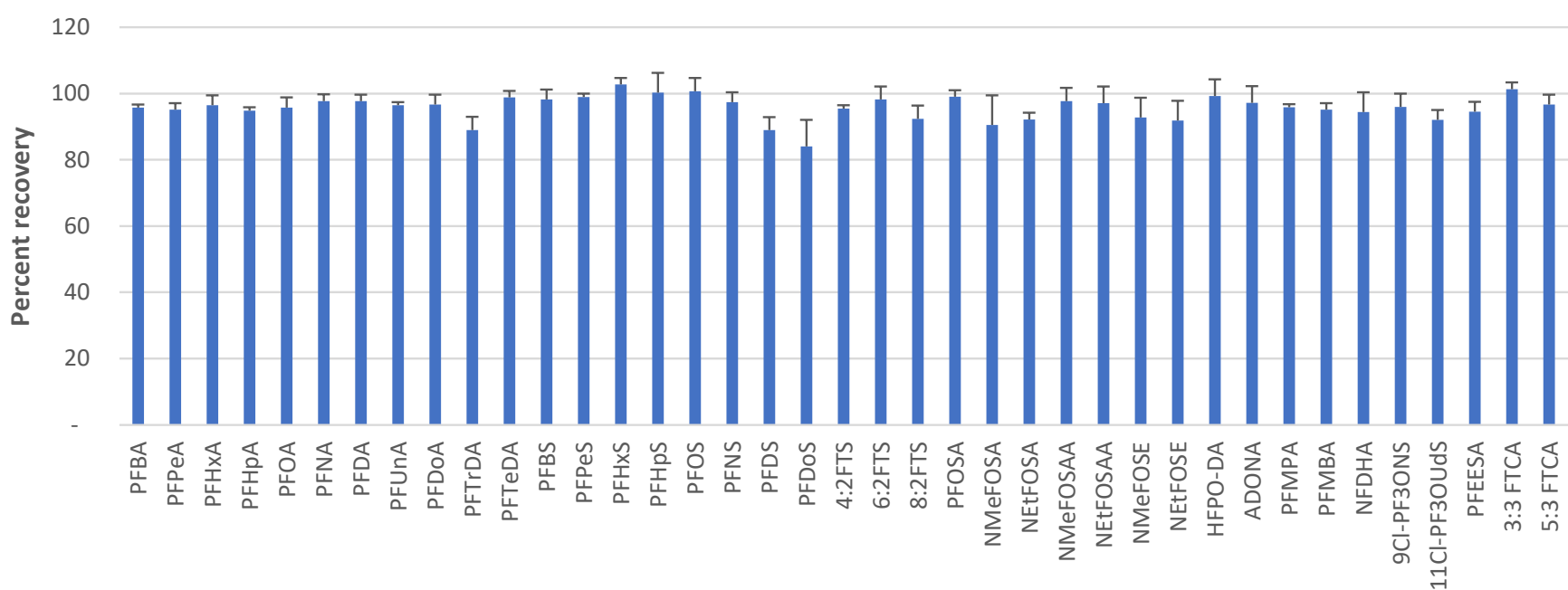
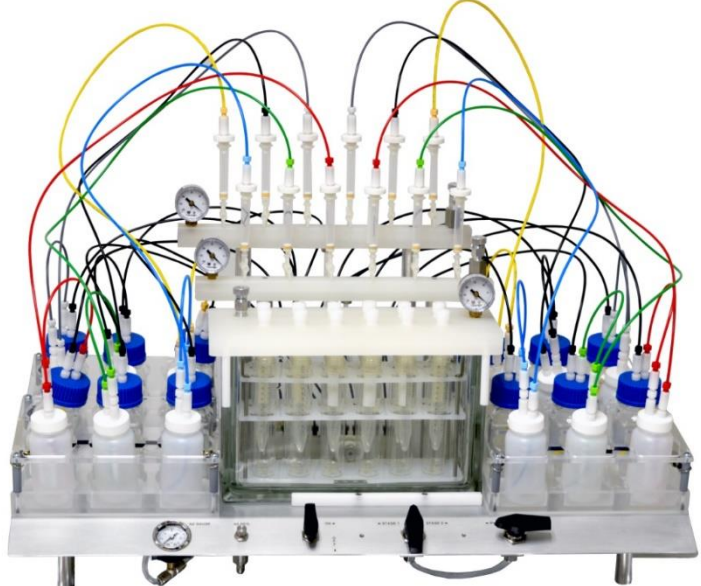


Figure 2. Recoveries of 40 native PFAS using the EZPFC semi-automated system.

Parallel/Sequential System



EZPFC

For additional information please contact:

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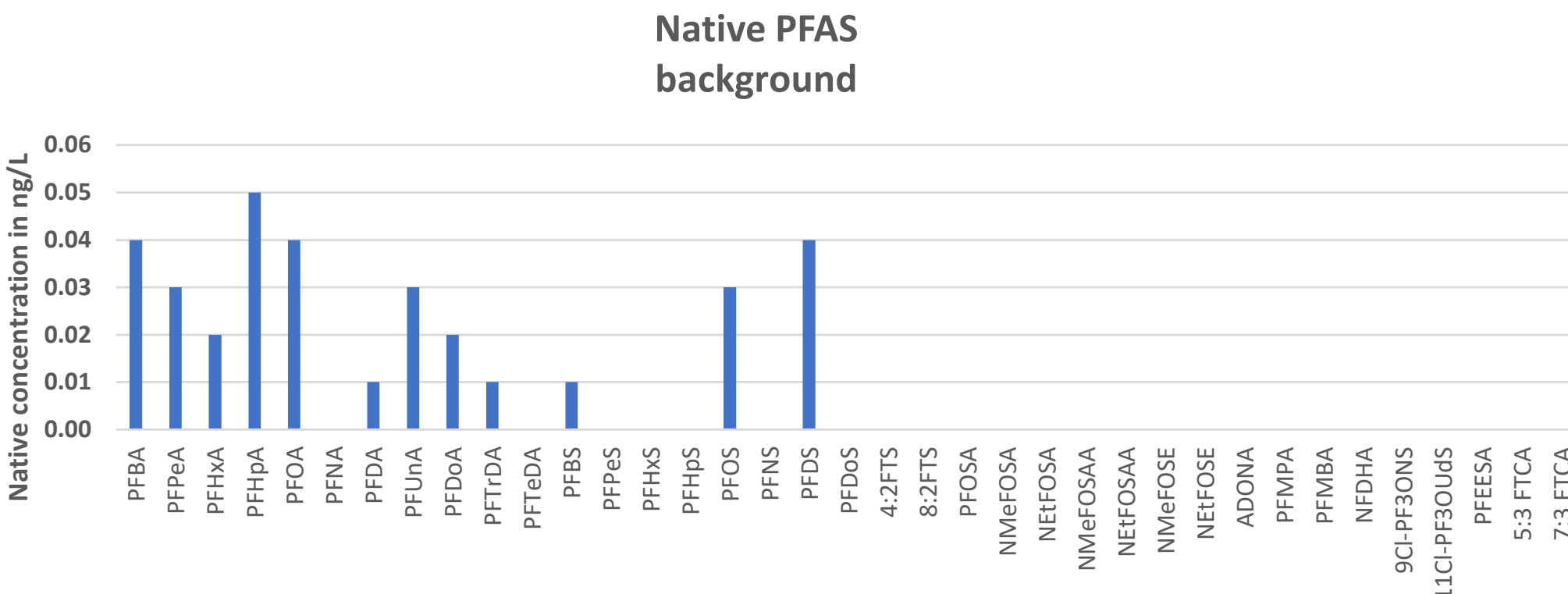


Figure 3. Native PFAS background contribution