

Analysis of Per- and Polyfluoroalkyl Substances in Drinking Water Using Sequential and Parallel Automated Solid Phase Extraction Using EPA Method 537.1

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- Perfluoralkylated compounds contain a perfluorinated or polyfluorinated carbon chain moiety such as $F(CF_2)_n$ - or $F(CF_2)_n-(C_2H_4)_n$.
- These make up a large group of persistent chemicals used in industrial processes and consumer applications:
 - Stain-Resistant Coatings for textiles and carpets
 - Grease-Proof Coatings for paper products approved for food contact
 - Firefighting Foams
 - Mining and Oil Well Surfactants
 - Floor Polishes
 - Insecticide formulations

Origin

- Industrial Sites
- Airport Fire Training Areas
- Wastewater Treatment Facilities
- Widespread use for over 60 years
- Very resistant to degradation
- Ubiquitous Compound in the Environment



- **Human exposure is linked to adverse effects**
 - Developmental issues in off-spring
 - Cancer
 - Immune system suppression
 - Endocrine disruption
 - Elevated levels of Cholesterol
 - Obesity



Source concerns

- Many water sources worldwide are found to be contaminated.
- Two compounds most studied:
 - Perfluorooctane sulphonate (PFOS)
 - Perfluorooctanoic acid (PFOA)
- Millions have been exposed through Drinking water supplies in the US and exceed the lifetime advisory of 70ng/L for these compounds



Regulation

- PFOS is now subject to varying but increasing levels of control in a number of countries.
- PFOA, also a widespread contaminant but with a far lower bioaccumulation potential, is still under evaluation.



The Analysis of PFAS

- Many of Thousands Samples are now being analyzed and more locations are starting to be analyzed for PFAS
 - Drinking Water
 - Waste Water
 - Human Serum
 - Biota
 - Soils



Challenges in the Analysis of PFAS

- The Analytical Systems are expensive
 - UPLC/MS systems
 - Require expertise in a new technology
- Manual Sample Prep processes
 - Inconsistent results
 - Elevated Background issues
 - Labor intensive
 - Extraction can take up to 2 hours
 - Concentration can take up to 2 hours





Optimizing the PFC Analysis Work Flow

- Automate the Sample Prep Workflow
 - Automate the Solid Phase Extraction Step
 - Automate the Concentration/Evaporation Step
- Automated SPE extractions and Concentration is a very green technique
 - Reduces Solvent Use
 - Reduces Solvent Disposal Costs
 - Reduces Solvent emissions
- FMS automated SPE systems deliver consistent, reproducible results
- Solid Phase Extraction is a well accepted technology

Reasons for SPE

- Reduced solvent
- Reduced glassware
- Simplified faster procedures (80 min automated vs 150 min manual)
- Automation versus manual protocols = Reproducibility



Determining Factors

- Ability to load samples by both positive pressure and vacuum.
- Ability to dry cartridges by both vacuum and positive gas pressure (N₂ or CO₂).
- Easily handle a wide variety of cartridge designs and sizes without cumbersome modifications.





Automated SPE System for PFAS extraction (1)



- Expandable from 1 to 6 modules
- Parallel and Sequential Extraction
- Direct to Concentrator and Vial
- All Inert Peek and Stainless Steel Surfaces



Automated SPE System for PFAS extraction (2)

- Low Background system
 - Peek and Stainless components
- Modular and Expandable System
 - Up to 6 modules
- High Throughput Runs Sample Extraction in Parallel and Sequential mode
- Up to 30 samples run unattended in 6 h period



Automated SPE System for PFAS extraction (3)

- Uses Vacuum for Sample Loading
- Uses Positive Pressure Pumping for Precise delivery of Elution and Wash Solvent





No Teflon



Extraction procedure (1)

- 250 mL water samples were spiked with 2 ng/L or 50 ng/L PFAS standards
- Uses FMS 500 mg - 1 g cartridge (DVB).
- Condition cartridge with 15 mL methanol.
- Condition cartridge with 18 mL water.



Extraction procedure (2)

- Load samples onto system
- Load samples across cartridges under -15 inches Hg vacuum (25-30 min)
- Rinse bottle with 2 x 7.5 mL of water and load onto the cartridge under negative pressure.



Extraction procedure (3)

- Dry cartridges under nitrogen until no residual water is present (5 min)
- Rinse the sample bottles and elute with 2 x 4 mL methanol





Automated SuperVap Evaporation

- Direct-to-Vial connections eliminate sample transfer
- Pre-heat temp: 50 °C
- Pre-heat time: 20 minutes
- Heat in Sensor mode: 50 °C
- Nitrogen pressure: 9 PSI
- The extracts were concentrated to 500 uL, add internal standard. The samples were diluted to a final volume of 1 mL with methanol for LC/MS analysis.



Analysis (1)

- **UPLC Conditions**

- Waters Acquity UPLC with Q-TOF (Xevo G2-XS) and HR-MS
- Acquity HSS T3 column (2.1 mm × 100 mm, 1.8 μm)
- Negative ESI

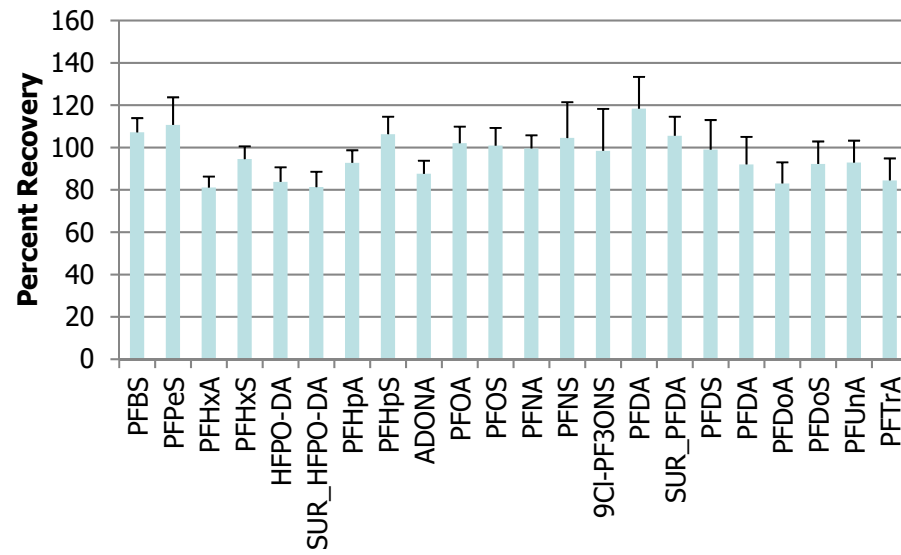


Analysis (2)

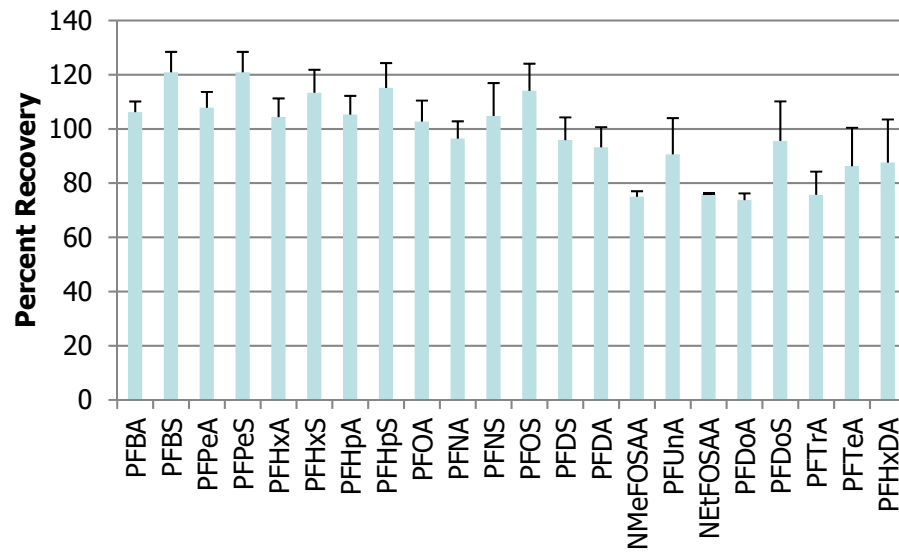
- **Solvent A:**
 - 0.1% formic acid in methanol
- **Solvent B:**
 - 0.1% formic acid in water



Recoveries 2 ppt PFAS

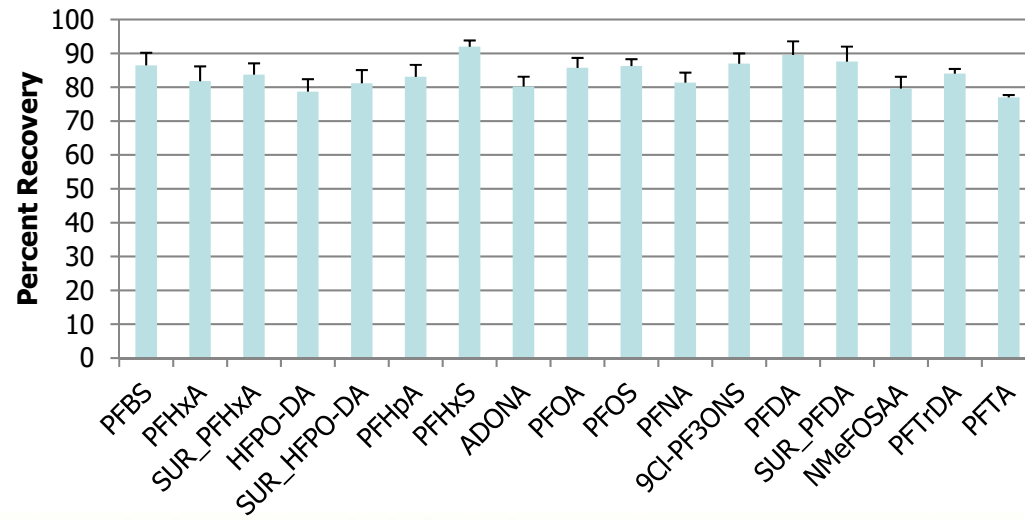


Recoveries 50 ppt PFAS

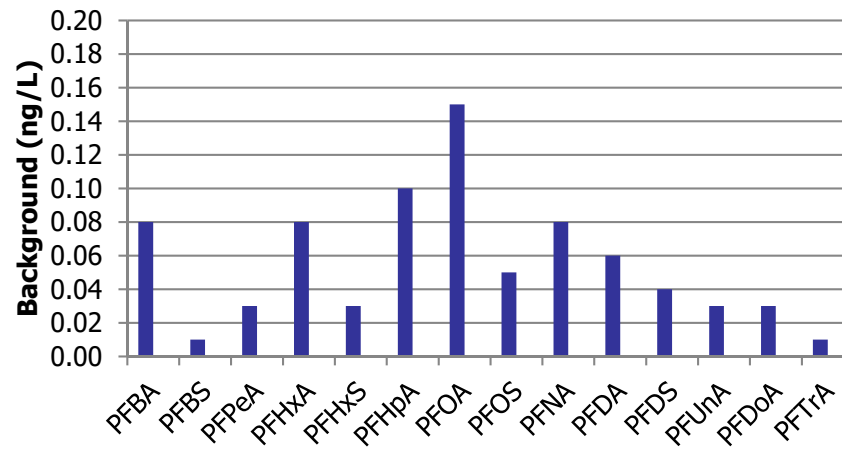




Recoveries 100 ppt PFAS



PFAS Background



Conclusions

- It is possible to automate the sample preparation of Per- and Polyfluoroalkyl Substances with the FMS SPE Parallel/Sequential System and SuperVap Concentrator for high throughput analysis
- Delivers consistent and reproducible results for PFAS analysis
- Can run up to 30 samples fully automated and unattended over a 6 h period
- The system, by design, has very low background PFAS allowing for analysis of samples without any significant interference.
- All models of FMS SPE systems are available as PFAS systems





Questions

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