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

Ruud Addink
Fluid Management Systems
Watertown MA

Introduction

- 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

Global Health concerns

- **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:
  - Perfluoroctane sulphonate (PFOS)
  - Perfluoroctannoic 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)

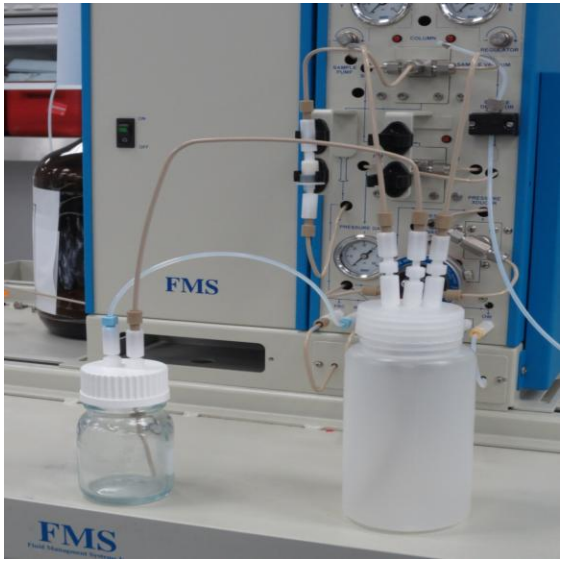
- Low Background system
  - Peek and Stainless components
- Modular and Expandable System
  - Up to 6 modules
- High Throughput Runs Sample Extraction in Parallel and Sequential mode
- Up to 30 samples run unattended in 6 h period

Automated SPE System for PFAS extraction (3)

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

Low PFAS Background

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 ^{O}C
- Pre-heat time: 20 minutes
- Heat in Sensor mode: 50 ^{O}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.

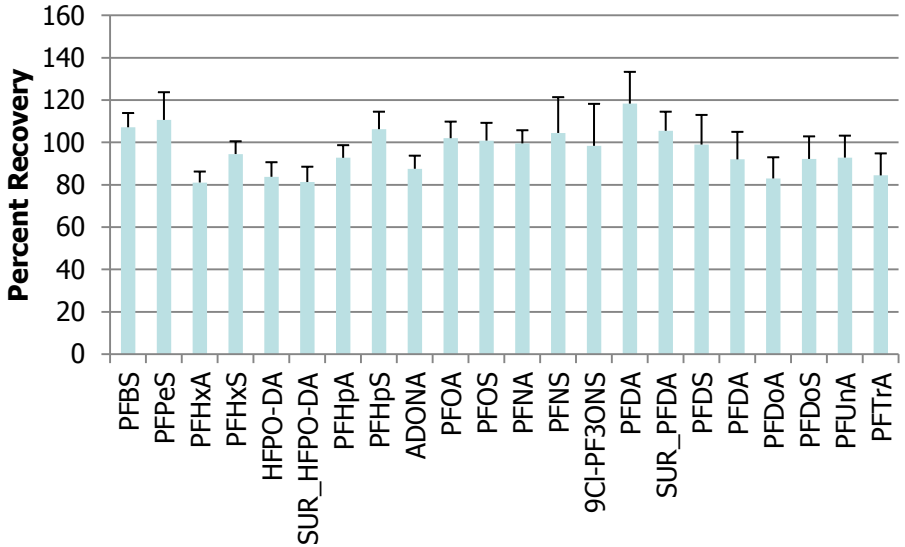
Analysis (1)

- **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

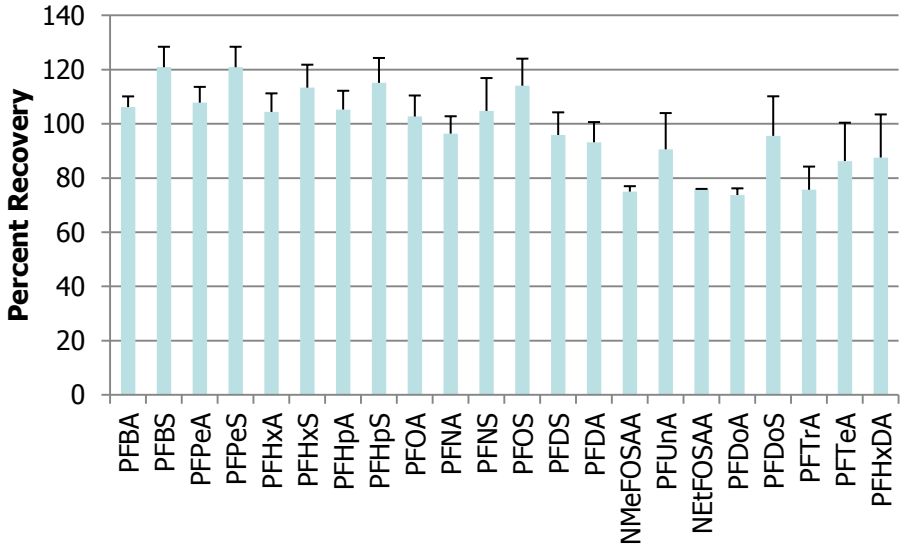
Analysis (2)

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

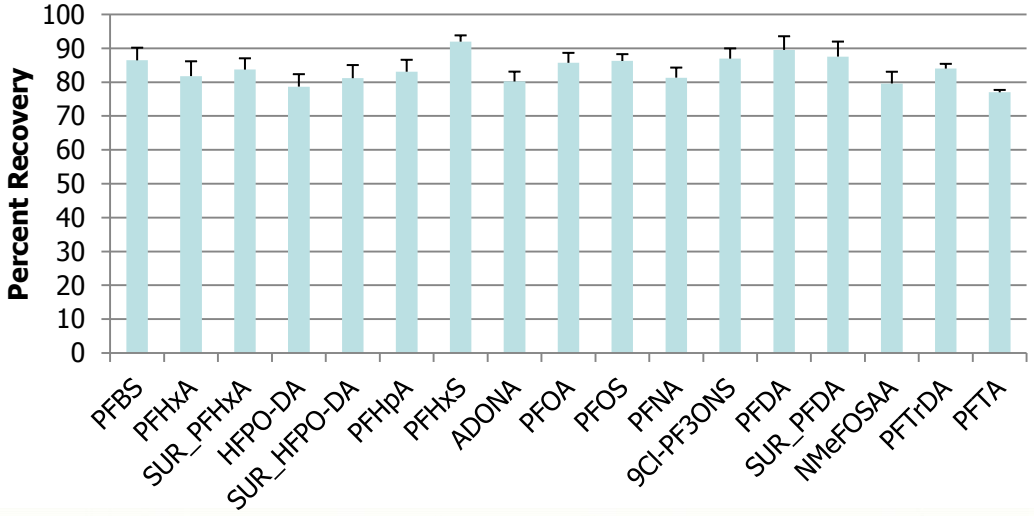
Recoveries 2 ppt PFAS



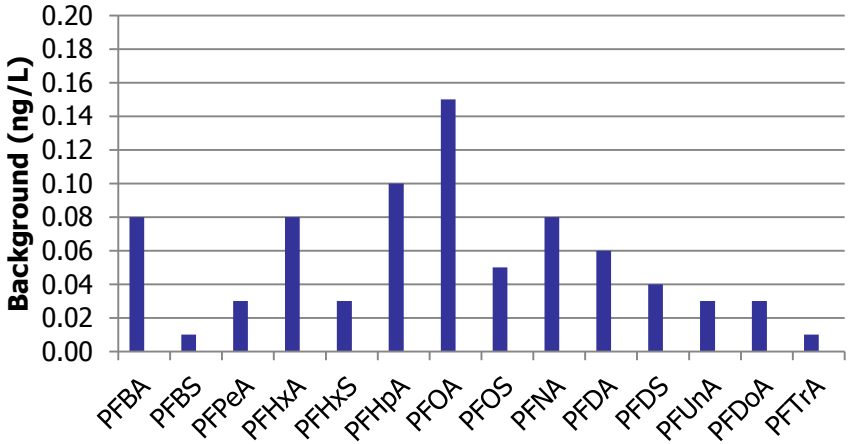
Recoveries 50 ppt PFAS



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

Contact us at:
raddink@fms-inc.com (Ruud Addink)
thall@fms-inc.com (Tom Hall)
nkaurin@fms-inc.com (Nem Kaurin)