Automated Low Background Solid Phase Extraction of Perfluorinated Compounds in Water

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
• 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
• 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.
Many of Thousands Samples are now being analyzed and more locations are starting to be analyzed for PFC’s

- Drinking Water
- Waste Water
- Human Serum
- Biota
- Soils
Challenges in the Analysis of PFCs

• 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 PFC extraction

- Expandable from 1 to 6 modules
- Parallel Extraction
- Direct to Concentrator and Vial
- All Inert Peek and Stainless Steel Surfaces
Automated SPE System for PFC extraction

- Low Background system
  - Peek and Stainless components

- Modular and Expandable System
  - Up to 6 modules

- High Throughput Runs Sample Extraction in Parallel
Automated SPE System for PFC extraction

- Uses Vacuum or Positive Pressure Pumping to Load Samples
- Uses Positive Pressure Pumping for Precise delivery of Elution and Wash Solvent
Lowering PFC Background

No Teflon
Extraction procedure (1)

- 500 mL water samples are spiked with 25 μL of 1 ug/mL PFC standard solution.

- Uses FMS 225mg cartridge.

- Condition cartridge with 15 mL methanol.

- Condition cartridge with 40 mL water.
• Load samples on the TurboTrace PFC SPE system.

• Pass across cartridge under -12 vacuum.

• Rinse bottle with 25 mL of water and loaded onto the cartridge under negative pressure.
Extraction procedure (3)

- Dry cartridges under nitrogen until no residual water is present
- Elute with 15 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, after which internal standard was added. The samples were diluted to a final volume of 1 mL of water for LC/MS analysis.
Analysis (1)

• UPLC Conditions

  – Waters Acquity H-Class UPLC

  – Column: Waters BEH C\textsubscript{18}, 2.1 x 50 mm, 1.7 um

  – Column temperature: 50 °C
Analysis (2)

- **Solvent A:**
  - (98:2) 2 mM Ammonium Acetate : Methanol

- **Solvent B:**
  - Methanol + 2 mM Ammonium Acetate
• Mass Spectrometer
• Ionization mode: ESI-
• Acquisition mode: Dual Scan MRM
• Capillary voltage: 0.44 kV
• Source: 150 °C
• Data: Acquisition and Analysis
PFCs Recoveries

![Graph showing percent recoveries of different PFCs]
PFCs Background

Blank concentrations (ng/L)

- PFPeA
- PFBS
- PFHxA
- PFHpA
- PFHxS
- PFOA
- PFNA
- PFOS
- PFDS
- PFDA
- PFUnA
- PFDoA
- PFTa
- PFTeA
Conclusions

- It is possible to automate the sample preparation of Perfluorinated Compounds with the FMS PFC SPE systems and SuperVap Concentrator for high throughput analysis.

- Delivers consistent and reproducible results for PFC analysis.

- The system, by design, has very low background PFC allowing for analysis of samples without any significant interference.

- All models of FMS SPE systems are available as PFC systems.

- Fully automated TurboTrace PFC System allows for rapid reliable same day analysis.