Automated Low Background Solid Phase Extraction of Perfluorinated Compounds in Water

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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 PFCs

- 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**

FMS
Fluid Management Systems

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 uL of 1 ug/mL PFC standard solution.**
- **Uses FMS 225mg cartridge.**
- **Condition cartridge with 15 mL methanol.**
- **Condition cartridge with 40 mL water.**

Extraction procedure (2)

- **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 ^{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, 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_{18}, 2.1 x 50 mm, 1.7 um
  - Column temperature: 50 ^{O}C

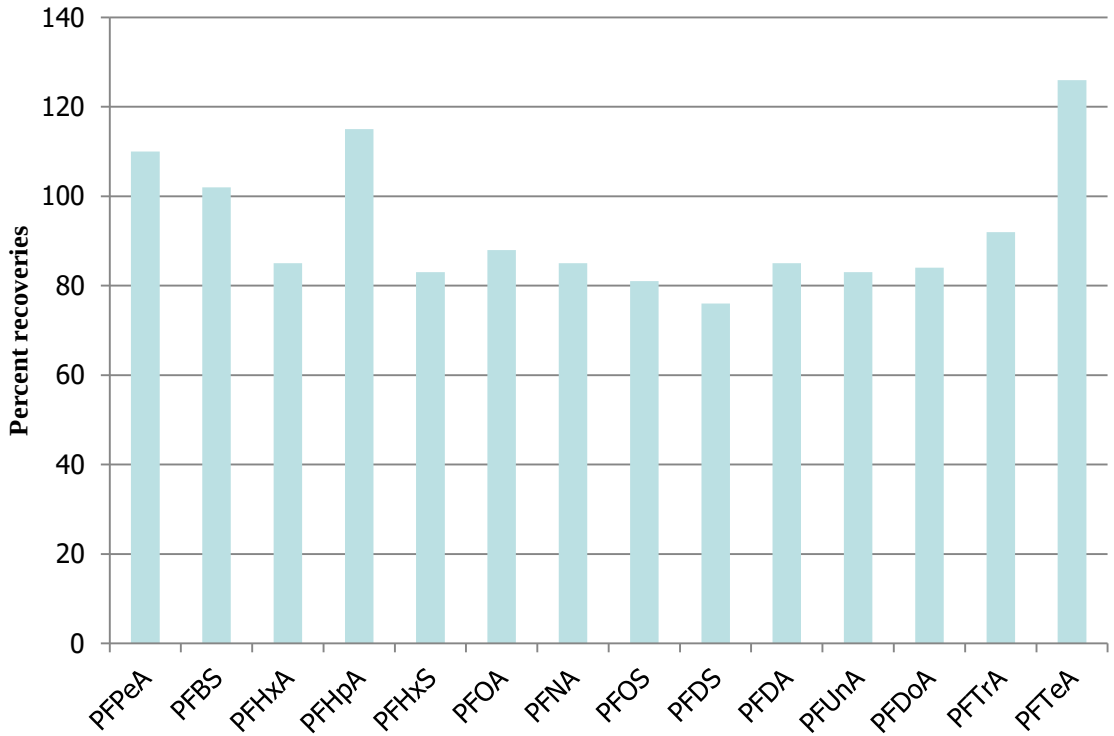
Analysis (2)

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

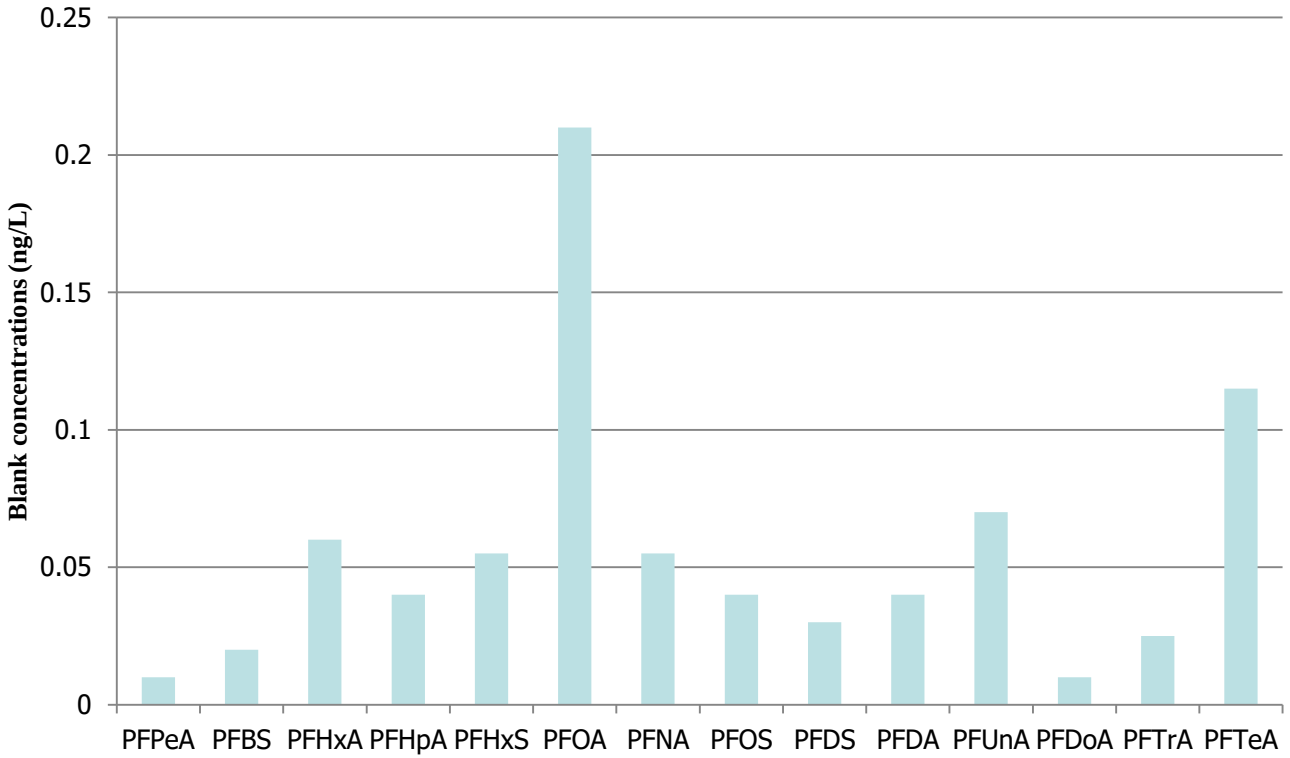
Analysis (3)

- **Mass Spectrometer**
- **Ionization mode: ESI-**
- **Acquisition mode: Dual Scan MRM**
- **Capillary voltage: 0.44 kV**
- **Source: 150 ^{o}C**
- **Data: Acquisition and Analysis**

PFCs Recoveries



PFCs Background



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**