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Analysis of Perfluorinated Compounds in Wastewater Using Automated Solid Phase Extraction

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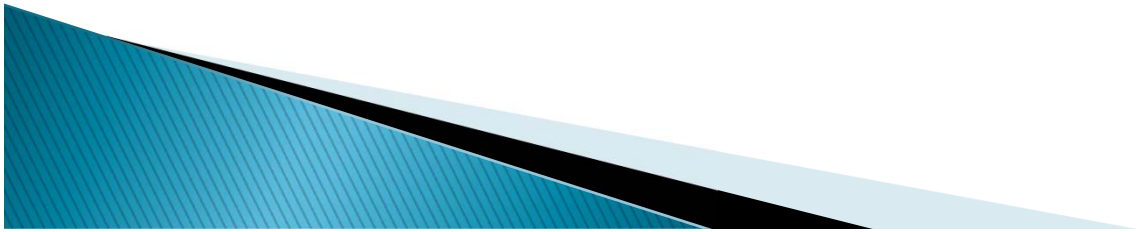
Introduction

- 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



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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

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Health Effects

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

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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.

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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

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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

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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

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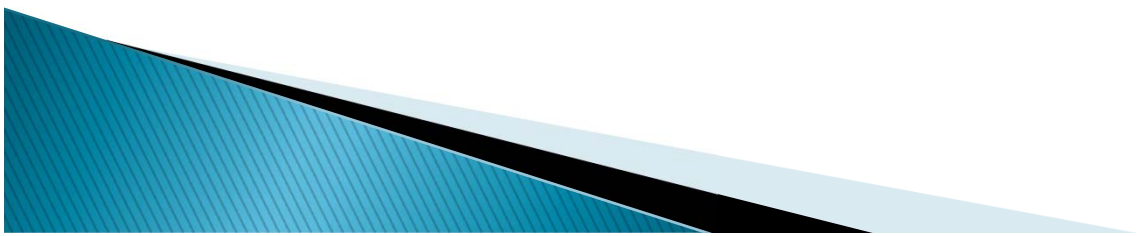
Reasons for SPE

- 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.



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Automated SPE System for PFC extraction (1)

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

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Automated SPE System for PFC extraction (2)

- Low Background system
  - Peek and Stainless components
- Modular and Expandable System
  - Up to 6 modules
- High Throughput Runs Sample Extraction in Parallel

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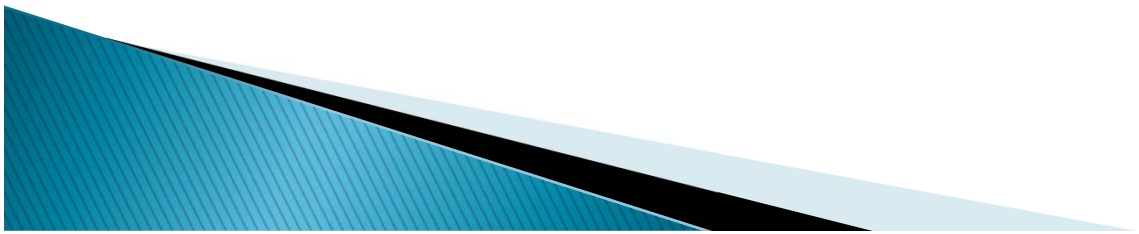
Automated SPE System for PFC extraction (3)

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



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Lowering PFC Background

No Teflon

Extraction procedure (1)

- 250 mL water samples are spiked with 25 uL of 1 ug/mL PFC standard solution.
- Uses FMS 225mg - 1 g cartridges.
- 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

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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

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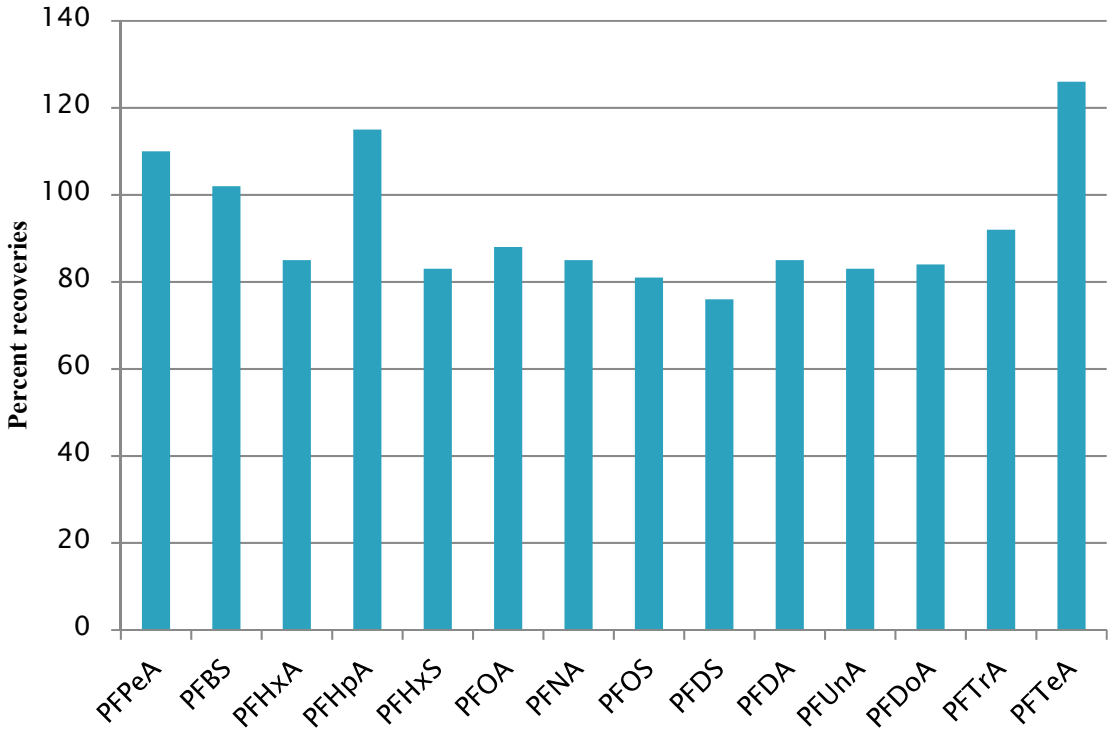
PFCs Recoveries (1)



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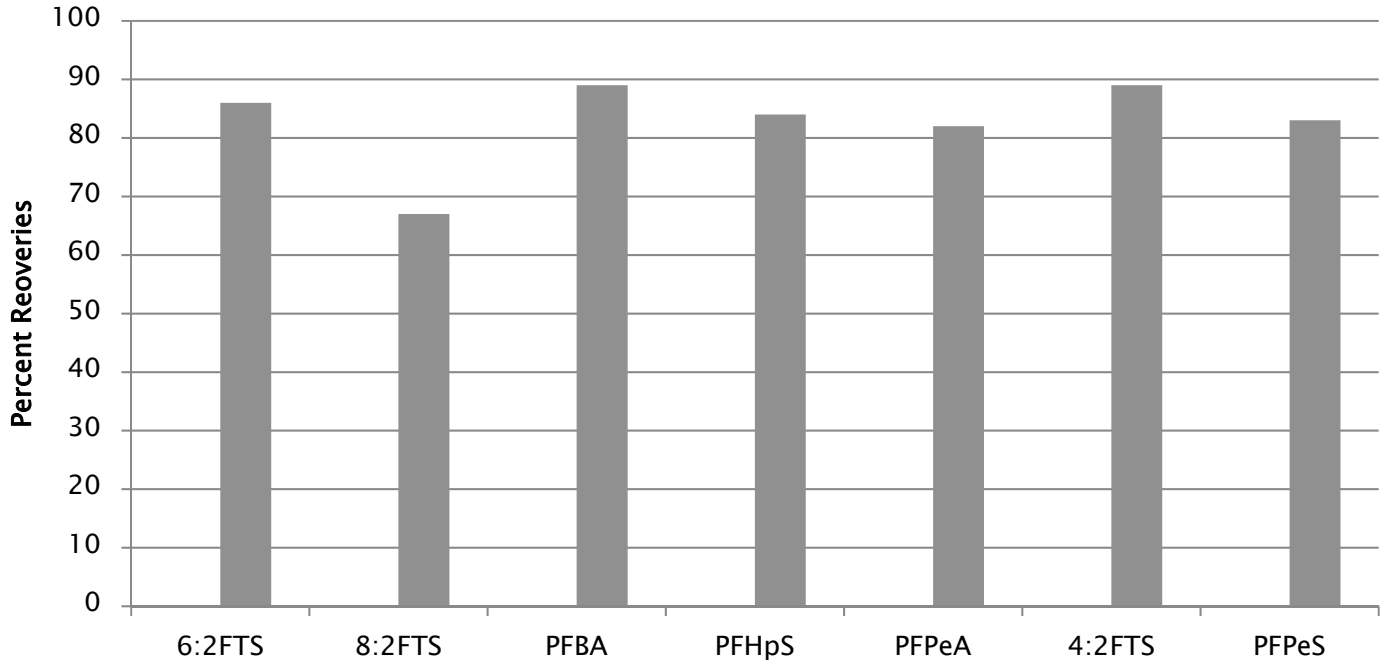
PFCs Recoveries (2)



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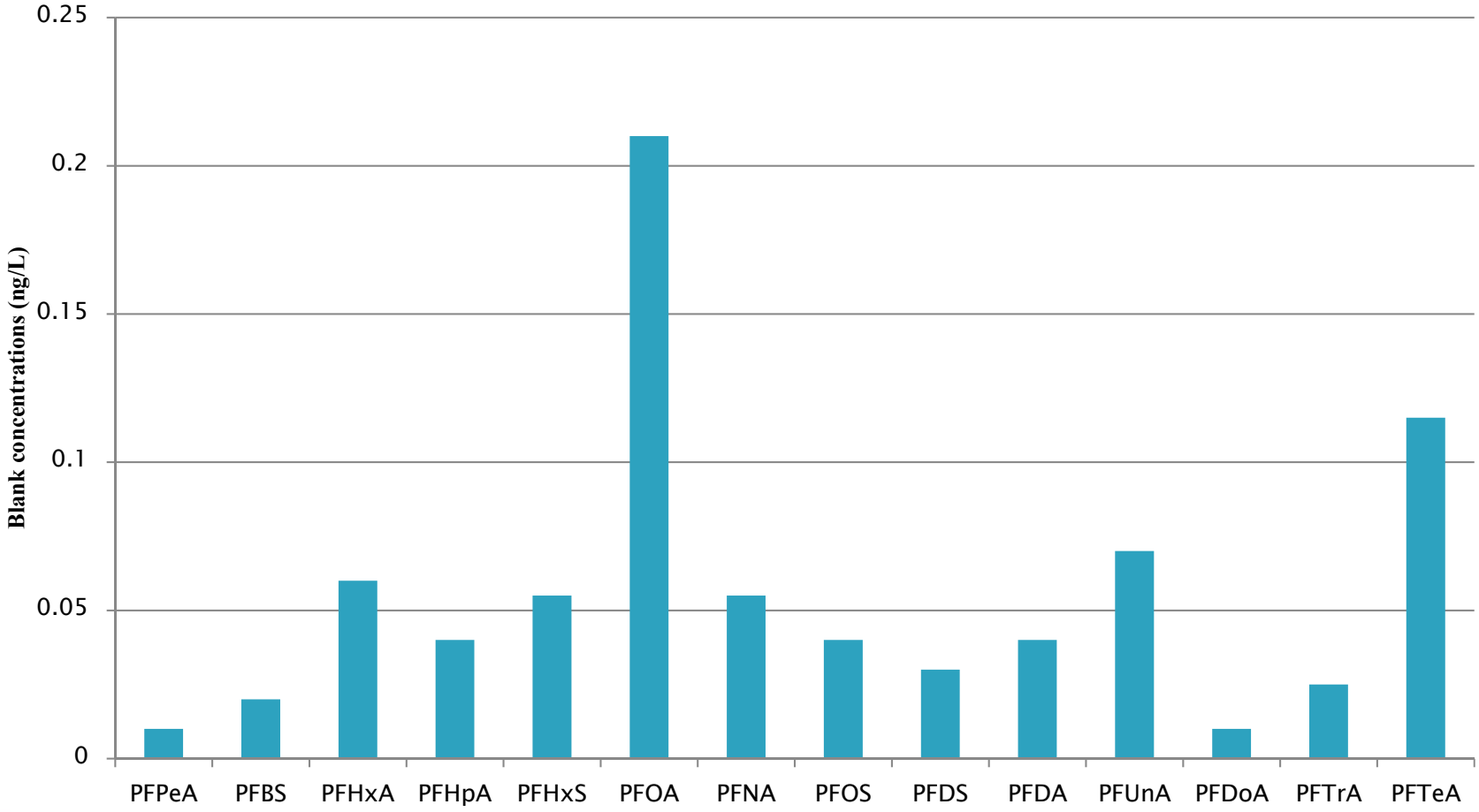
PFCs Background



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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 of waste water