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(CF₂)ₙ or F(CF₂)ₙ-(C₂H₄)ₙ.

- Use in industrial 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; and insecticide formulations.

- Concern over levels in the global environment: fate and possible adverse effects.
• **Results from animal studies:**
  – Disruption of endocrine activity.
  – Reduced immune function.
  – Damage to liver and pancreas.
  – Developmental problems in off-spring.
Health concerns (2)

- Data from human studies have been contradictory: some found effects on human health, some did not.
- Additional work is needed.
- Two compounds most studied: perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA).
Health concerns (3)

- These are final environmental degradation products of (and contaminants in) a wide range of other perfluorinated products and have therefore been of most interest.
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.
SPE System for PFC extraction
Extraction procedure (1)

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

- Use Waters HLB Plus 225mg cartridge.

- Condition cartridge with 15 mL methanol.

- Condition cartridge with 40 mL water.
Extraction procedure (2)

- Load samples on the FMS PFC SPE system.
- Pass across cartridge under -12 psi vacuum.
- Rinse bottle with 25 mL of water and load onto the cartridge under negative pressure.
Extraction procedure (3)

- Dry cartridges under nitrogen until no residual water is present (~ 20 min).

- Elute with 15 mL methanol.
12 position evaporator
SuperVap Evaporation

- 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 μL, after which internal standard was added. The samples were diluted to a final volume of 1 mL of water for LC/MS analysis.
Waters Acquity H-class LC and Xevo TQ MS.
• **UPLC Conditions**

  - Waters Acquity H-Class UPLC
  - Column: Waters BEH C$_{18}$, 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
Analysis (3)

- Xevo TQD mass spectrometer
- Ionization mode: ESI-
- Acquisition mode: Dual Scan MRM
- Capillary voltage: 0.44 kV
- Source: 150 °C
- Data: acquisition and analysis using MassLynx v.4.1 software
## Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount Spiked ng/L</th>
<th>Mean Percent Recovery</th>
<th>Background from FMS SPE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perfluorinated Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHxA</td>
<td>50 ng/L</td>
<td>61%</td>
<td>0.068</td>
</tr>
<tr>
<td>PFHxS</td>
<td></td>
<td>77%</td>
<td>0.06</td>
</tr>
<tr>
<td>PFOA</td>
<td></td>
<td>88%</td>
<td>0.214</td>
</tr>
<tr>
<td>PFNA</td>
<td></td>
<td>74%</td>
<td>0.062</td>
</tr>
<tr>
<td>PFOS</td>
<td></td>
<td>72%</td>
<td>0.048</td>
</tr>
<tr>
<td>PFDA</td>
<td></td>
<td>84%</td>
<td>0.054</td>
</tr>
<tr>
<td>PFUdA</td>
<td></td>
<td>65%</td>
<td></td>
</tr>
<tr>
<td>PFDoA</td>
<td></td>
<td>57%</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Conclusions

• It is possible to automate the sample preparation of Perfluorinated Compounds with the FMS PFC SPE system to get reliable and reproducible results for perfluorinated compounds in water.

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

• Fully automated features make for rapid and reliable sample processing with same-day-analysis.