ANALYSIS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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INTRODUCTION: PFAS IN THE NEWS

Drinking Water Health Advisories for PFOA, PFOS

70 ng/L: individually or in combination

What is a ng/L?

- 1 drop in 13,208,600 gallons

70 ng/L = 3.5 drops
**Perfluoroalkyl carboxylates:**

Examples:
- $m=2$ PFBA
- $m=4$ PFHxA
- $m=6$ PFOA

**Perfluoroalkane sulfonates:**

Examples:
- $m=3$ PFBS
- $m=5$ PFHxS
- $m=7$ PFOS

*Per = fully fluorinated alkyl tail.*
INTRODUCTION: TERMINOLOGY & STRUCTURE

**Perfluoroalkyl carboxylates:**
- Examples:
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  - \( m=6 \) PFOA

**Perfluoroalkane sulfonates:**
- Examples:
  - \( m=3 \) PFBS
  - \( m=5 \) PFHxS
  - \( m=7 \) PFOS

**Polyfluoroalkyl substances:**
- \( m=5 \ 6:2 \ FtS
- \( m=7 \ 8:2 \ FtS

Poly = partially fluorinated alkyl tail.
INTRODUCTION: TERMINOLOGY & STRUCTURE

**Perfluoroalkyl carboxylates:**

Examples:
- $m=2$ PFBA
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- $m=6$ PFOA

**Perfluoroalkane sulfonates:**

Examples:
- $m=3$ PFBS
- $m=5$ PFHxS
- $m=7$ PFOS

**Per** + **Poly** = **Per & polyfluoro alkyl substances (PFAS)**

**Polyfluoroalkyl substances:**

- $m=5$ 6:2 FtS
- $m=7$ 8:2 FtS
**Poly**fluoroalkyl substances that can undergo transformation to form **per**fluoroalkyl acids

**INTRODUCTION: TERMINOLOGY & STRUCTURE**

What is a precursor?

*Poly*fluoroalkyl substances that can undergo transformation to form **per**fluoroalkyl acids

PFHxSA

(Precursor)

where \( n = 6 \)

FHxSA (Intermediate precursor)

PFHxS
INTRODUCTION: CHEMISTRY AND USES³

PFAS characteristics:
• Chemically stable
• Thermally stable
• Hydrophobic/lipophobic
• Surfactant properties
• Recalcitrant in environment

PFAS Uses:
• Fluoropolymer manufacturing (e.g. polytetrafluoroethylene)
• Firefighting foams
• Electroplating, paper coating, stain/water repellant, textiles, electronics, insecticides/herbicides, adhesives, etc.
OVERVIEW

• Sample preparation
• Sample analysis
• Laboratory QA/QC
• Standard methods
• Commercial labs
• Novel analytical tools
• Summary

You have your sample, now what?
SAMPLE PREPARATION

Solids extraction:
- Soils, plants, other biological tissue
- No direct analysis of solids
- Use solvent to extract compound off of solid, analyze extract
- Extraction methods vary

Ex: Soil + organic solvent, heat & shake
SAMPLE PREPARATION

Solids extraction:
- Soils, plants, other biological tissue
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- Extraction methods vary

Solid phase extraction (SPE):
- Load large volume onto cartridge, elute off into smaller, cleaner volume
- Concentrates sample
- Not always needed- direct, large volume injection
- Some methods use it, some do not
ANALYSIS: LC-MS/MS OVERVIEW

Liquid chromatography tandem mass spectrometry (LC-MS/MS)

High performance liquid chromatography (HPLC)

HPLC system control

Desktop Computer

MS/MS system control

Tandem mass spectrometer (MS/MS)

Ionizing Interface (source)
Quadripole 1 (Q1) Analyzer
Q2 Collision Cell
Quadripole 3 (Q3) Analyzer
Ion detector

Auto-sampler

Valve

Sample Injection

HPLC Pump

Controller

Mobile phases
ANALYSIS: LC-MS/MS OVERVIEW

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Quadripole 3 (Q3) Analyzer

Ion detector
ANALYSIS: LC-MS/MS OVERVIEW

HPLC Separation

- Separates compound mixtures
- Characteristic retention times
- Step 1 in compound ID

MS/MS Detection

- Unique fragmentation patterns
- Parent-daughter combos = definitive ID, sensitive analysis

Parent ionized

MS1: analyzes parent mol. wt.

Collision cell: parent fragmentation

MS2: analyzes daughter mol. wt

Accepted tool for PFAS analysis
Data analysis/quantification:
• Generally, concentrations determined by comparison of compound response to calibration curve
• Exact method of quantifying concentration may differ between labs
• Examples: external calibration, internal standard, isotope dilution
QUALITY ASSURANCE/QUALITY CONTROL

**Method blanks:** checks for contamination during sample preparation; ~2/30 samples + after elevated samples

**Laboratory control:** adds known amt. compound to clean matrix; ensures test method is working; ~1/30 samples

**Matrix spike:** adds known amt. compound to field sample; tests matrix interferences; ~1/30 samples

**Duplicate:** tests analytical precision; ~1/30 samples

**Calibration check:** Validates existing calibration; frequency varies e.g. 1/10 samples and at batch end for EPA 537

10 ng/L
### STANDARD METHODS FOR PFAS

<table>
<thead>
<tr>
<th>Method Name</th>
<th>Method 537</th>
<th>ASTM D7979-16</th>
<th>ASTM D7968-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Drinking water</td>
<td>Water, influent/effluent wastewater, sludge</td>
<td>Soil</td>
</tr>
<tr>
<td>Compound Classes</td>
<td>PFAA, FASAA</td>
<td>PFAA, n:3 acid, FTUCA, FTCA</td>
<td>PFAA, n:3 acid, FTUCA, FTCA</td>
</tr>
<tr>
<td>Sample container</td>
<td>Polypropylene</td>
<td>Polypropylene</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Sample volume</td>
<td>250 mL</td>
<td>5 mL</td>
<td>2g, adjust if needed</td>
</tr>
<tr>
<td>Extraction</td>
<td>SPE</td>
<td>None</td>
<td>50:50 H₂O: MeOH</td>
</tr>
<tr>
<td>Filtering</td>
<td>None</td>
<td>Polypropylene</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Reporting Limits</td>
<td>2.9-14 ng/L</td>
<td>10-300 ng/L</td>
<td>25-750 ng/kg</td>
</tr>
<tr>
<td>Holding Times</td>
<td>14 days</td>
<td>28 days</td>
<td>28 days</td>
</tr>
<tr>
<td>Preservation</td>
<td>5 g/L buffer, cooled &lt;10°C</td>
<td>Cooled, &lt;6°C</td>
<td>Cooled, &lt;6°C</td>
</tr>
<tr>
<td>Quantification</td>
<td>Internal std.</td>
<td>External cal.+ recovery of isotope labeled PFAS</td>
<td></td>
</tr>
</tbody>
</table>

- PFAA = perfluoroalkyl acids
- FASAA = perfluoroalkyl sulfonamidoacetic acid
- n:3 acid = n:3 saturated acid
- FTUCA = fluorotelomer unsaturated carboxylic acid
- FTCA = fluorotelomer carboxylic acid
## COMMERCIAL LAB AVAILABILITY

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Method</th>
<th>Matrices</th>
<th>Compound Classes</th>
<th>Aqueous RL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axys</td>
<td>Internal</td>
<td>Water, Solid, Air, Tissue, Serum, Urine</td>
<td>PFAA, FTS, FASA, FASAA, PAP, FTCA</td>
<td>1-80 ng/L</td>
</tr>
<tr>
<td>Eurofins</td>
<td>EPA 537 or direct injection</td>
<td>Water, Solid, Tissue, Products</td>
<td>PFAA, FTS, FASAA</td>
<td>2-10 ng/L</td>
</tr>
<tr>
<td>Test America</td>
<td>Mod EPA 537</td>
<td>Water, Solid</td>
<td>PFAA, FTS, FASA, FASAA, FASE</td>
<td>2-100 ng/L</td>
</tr>
<tr>
<td>Vista</td>
<td>Mod EPA 537</td>
<td>Water, Solid, Tissue</td>
<td>PFAA, FTS, FASA, FASE, FASAA</td>
<td>1-40 ng/L</td>
</tr>
</tbody>
</table>

* Reporting limit (RL) range encompass all compound classes; RLs for all labs were below EPA HA levels for PFOS/PFOA

- PFAA = perfluoroalkyl acids
- FTS = fluorotelomer sulfonates
- PAP = polyfluoroalkyl phosphate esters
- FASA = perfluoroalkyl sulfonamides
- FTCA = fluorotelomer carboxylic acid
- FASE = perfluoroalkyl sulfonamidoethanol
- FASAA = perfluoroalkyl sulfonamidoacetic acid
- FTUCA = fluorotelomer unsaturated carboxylic acid
Total oxidizable precursor assay:

Add:
60 mM $\text{K}_2\text{S}_2\text{O}_8$
125 mM NaOH

React:
6 hrs
85° C

Heated oxidative conversion

$\text{PFCAs}_0 + \text{PFSAs}$

Precursors

$\text{PFAA}_{\text{final}} - \text{PFAA}_0$

$\text{PFCAs}_{\text{final}} + \text{PFSAs}$

Bulk precursor quantification = total amt. precursors present
Does not identify individual precursor compounds present
OTHER ANALYTICAL TOOLS: PIGE

Particle induced gamma-ray emission (PIGE):

- Spectroscopic measurement of $^{19}\text{F}$ nuclei
- Measures *total* fluorine- helping to complete PFAS mass balance
- Applicable to soil, products (e.g. paper), geologic formations, etc.
Summary

- Primary tool for detection/quantification: LC-MS/MS
- Sample extraction/preparation techniques vary
- Commercial availability of compound classes/matrices varies
- High potential for background issues → QA/QC!

In the future

- Diversification of target compounds
- Need for comparison across labs/methods
- Commercial development of novel techniques (e.g. TOP)
REFERENCES


