PER- AND POLYFLUORORALKYL SUBSTANCE DARK MATTER

Role of Total Organofluorine Analysis
• Per- and Polyfluorinated Alkyl Substances (PFAS)
  • History
  • Environmental Concern
  • PFAS “Dark Matter”

• Total Organic Fluorine: TOF
  • Combustion Ion Chromatography
  • What do the results mean compared to specific PFAS?
  • Benefits of knowing TOF

• Bureau Veritas Laboratories and TOF
  • Description of Service Offering
    “where we’re at and where we’re going”
WHEN YOU THINK PFAS, THINK...

- PFOA
- PFOS
MAJOR SOURCES OF PFAS IMPACT

- Fire training/response sites
  - AFFF inventories
  - AFFF releases

- Industry
  - Dupont ↔ Chemours
  - 3M
  - 3rd party manufacturers

- Wastewater treatment plants
  - Biosolids

- Landfills
  - Historic impacts
ENVIRONMENTAL INTEREST IN PFAS

Where it began…

**Perfluorooctanoic Acid (PFOA)** ≈ “Teflon®”

**Perfluorooctanesulfonic Acid (PFOS)** ≈ “Scotchguard®”

**Perfluorobutanoic Acid (PFBA)**

**Perfluorononanoic Acid (PFNA)**

Precursors

**6:2 Fluorotelomersulfonic Acid (6:2 FTS)**

**8:2 Fluorotelomer Alcohol (8:2 FTOH)**

**6:2 Fluorotelomesulfonamide (PFOSA)**

**N-Ethylperfluorooctanesulfonamidoacetic Acid (EtFOSAA)**

Replacements

**2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX)**

**9-Chlorohexadecafluoro-3-oxanone-1-sulfonate (F53B major)**

**11-Chlororeicosafluoro-3-oxaundecane-1-sulfonic Acid (F53B minor)**

**Dodecafluoro-3H-4,8-dioxanoate (ADONA)**

Environmental Conversion

4000+ Compounds (“Dark Matter”)
PFAS “DARK MATTER”

• Typical PFAS analyses report 20-50 PFAS
• It is well understood that there are thousands of PFAS compounds present in the environment, most are unknown or uncharacterized:

The Dark Matter

• PFAS Dark Matter can:
  - Break down or transform into PFAS that are measured
  - Contribute toxicity risk beyond that identified by the currently reported PFAS
• How do you accurately assess site risk or required remedial effort with this unknown?
• The Total Oxidizable Precursors (TOPs) assay gave us a glimpse of the Dark Matter but most now agree it is not a full solution.
  - Not fully quantitative
  - High sample variability.
  - Does not necessarily capture all of the Dark Matter

The answer… Total Organic Fluorine (TOF)
OPTIONS FOR TOTAL ORGANOFUORINE ANALYSIS

**CIC**: Combustion Ion Chromatography
Uses equipment similar to that in wide use in Europe for ‘Adsorbable Organic Halides’ (AOX) analysis.

**PIGE**: Particle-Induced Gamma Ray Emission Spectroscopy
Uses equipment available to only a few laboratories with access to suitably-equipped research facilities.

**INAA**: (Instrumental) Neutron Activation Analysis
Uses equipment available only to laboratories with access to a research grade nuclear reactor – Including Bureau Veritas

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**Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?**

PFAS – BUREAU VERITAS OPTIONS

Where it began...
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4000+ Compounds ("Dark Matter")

Environmental Conversion

PFAS by LC-MS/MS
PFAS + “Dark Matter” by TOPs Assay
Total Organic Fluorine by Combustion Ion Chromatography
Determination of adsorbable organically bound fluorine (AOF) and adsorbable organically bound halogens as sum parameters in aqueous environmental samples using combustion ion chromatography (CIC)

Total Organofluorine vs Σ PFAS in Wastewater

- Semi-automated SPE
  - Isolate organofluorine from inorganic fluorine
- Automated combustion
  - Organofluorine converted to HF and trapped in water.
- Automated transfer to ion chromatograph.
- Total organofluorine in wastewater typically 100x higher than sum of PFAS suggests.


Method described in Thermo Scientific Application Note 73481
BUREAU VERITAS LABORATORIES’ CIC-TOF SYSTEM

#1 PFAS Adsorption

#2a Combustion Autosampler

#2b Combustion Unit

#3 HF Absorption

#4 Ion Chromatograph
WHAT DO TOF RESULTS MEAN?

Remember…

TOF by CIC is measuring the **fluorine contribution** from all of the fluorine-containing compounds in the sample

![PFOS structure](image)

PFOS (C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>−)

**PFOS Mol. Wt.** = 499 g/mol

**F Mol Wt.** = 19 g/mol

17x F = 323 g/mol

**Fluorine Contribution:** \( \frac{323}{499} = 64.7\% \)

Measured amounts…

PFOS (by LC/MS/MS) = 250 ng/L PFOS

\[ F_{\text{total}} \text{(by CIC)} = 0.647 \times 250 \text{ ng/L} \]

\[ = 162 \text{ ng/L F} \]

~65%
LC-MS/MS vs. CIC-TOF: WATER SAMPLES

Field Blank

Sample reported by LC-MS/MS
✓ 0.07 µg/L ΣPFAS
✓ 0.002 µg/L PFOS
i.e. meets all proposed regulatory requirements.

TOF result: 2.1 µg/L

CIC-TOF DL: 2 µg/L (due to F background from SPE carbon)
LC-MS/MS vs. CIC-TOF: WATER SAMPLES

CIC DL: 2 µg/L (due to F background from SPE carbon)
**Supplier Information:**

“XXX is readily biodegradable and virtually nontoxic to aquatic organisms. It is based on a natural protein foaming agent and contains no harmful synthetic detergent… XXX can be successfully treated in biological wastewater treatment systems.”
ANTICIPATED BENEFITS OF CIC-TOF

1. Increased reliability of PFAS impact delineation
2. Simplified AFFF evaluation
3. Increased accuracy in estimating required remedial effort and costs
4. Improved monitoring of remedial progress
5. Reduced cost
6. Faster turn-around
PFAS ANALYSIS TOOLKIT

1. PFAS by LC-MS/MS
   - Report specific PFAS chemicals with low reporting limits - $$
   - Complies with EPA 537m
   - Bureau Veritas Accreditation in all of Canada and many US states.

2. TOPs Assay
   - Report specific PFAS chemicals with low reporting limits – BEFORE & AFTER oxidizing sample to simulate natural processes - $$$
   - Analysis complies with EPA 537m
   - Bureau Veritas Accreditation in all of Canada and many US states.

3. TOF by CIC
   - Report total organofluorine from ‘all’ PFAS in the sample - $
   - No current EPA method or industry standards for testing… yet.
   - Validated according to ISO 9562:2014 and Thermo Application Note
   - Bureau Veritas Accreditation through Standards Council of Canada (SCC)
WHEN TO USE WHICH TOOLS?

**TOPs Assay**
- Mimics natural oxidation processes
- Get *Indication* of total PFAS contamination
- Low reporting limits (<µg/L)

**TOF by CIC**
- Measure total PFAS contamination
- Product testing *Is my product “PFAS-free”?*
- Moderate reporting limits: 2 µg/L
- Liability risk assessment

**PFAS by LC-MS/MS**
- Accurate low level measurement of individual compounds (<µg/L)
- Regulatory compliance
- Health risk assessment
SAMPLE SUBMISSION INFORMATION

Bottles:
- **Waters**: 250 mL polypropylene, same as for PFAS soils, pre-charged with nitric acid preservative.
- **AFFF**: 125 mL polypropylene, same as for PFAS waters, unpreserved

Hold Times:
- **Waters**: 28 days, refrigerated
- **AFFF**: indefinite, refrigerated

TAT:
- Regular: 10 days
- Rush: 3 days

Reporting Limit:
- Water: 2 µg/L
WHAT HAVE WE LEARNED ABOUT SAMPLING?

- Strict/rigorous sampling protocols
- Have a solid QA program
- Sample containers must be PFAS-free
- Water for QC purposes must be PFAS-free
- Consider unexpected PFAS sources during sampling:

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<th>Prohibited</th>
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<tr>
<td>Waterproof field books</td>
<td>Aluminum clipboards; Loose paper</td>
<td>Post-it Notes®</td>
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<tr>
<td>Water and dirt resistant leather gloves</td>
<td>Powderless nitrile gloves</td>
<td>Off-brand markers</td>
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<td>Decon 90</td>
<td>Alconox®, Liquinox® or Citrinox®</td>
<td>Any special gloves/clothing required as specific personal protective equipment (PPE)</td>
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<tr>
<td>Chemical or “Blue” ice</td>
<td>Regular ice (sealed polyethylene bags)</td>
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PHASE I
Commercialized CIC-TOF method. Water and AFFF Only

- Equipment set-up - Complete
  - Equipment installation
  - Method set-up – published method

- Method validation
  - Determine method detection limits – anticipate <5 ppb
  - Determine precision & accuracy

- Educational Materials
  - Technical Bulletins, Sales Sheets, etc.
  - Case Studies
  - Presentations

PHASE II
Optimize and extend method

- Extend method
  - Soils
  - Etc…

- Reduce DL
  - Increase sample volume
  - Improved instrument precision

- Improve recovery
  - Especially high MW PFAS

- Shorten run times – higher throughput
  - Increase sample prep capacity
  - Reduce CIC run time
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