PER- AND POLYFLUOROALKYL SUBSTANCE DARK MATTER

Role of Total Organofluorine Analysis

OUTLINE

- 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…

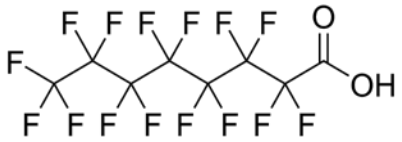
PFOS

MAJOR SOURCES OF PFAS IMPACT

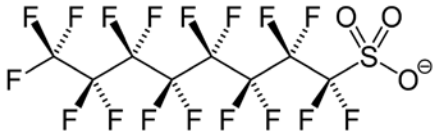
- Fire training/response sites
  - *AFFF inventories*
  - *AFFF releases*
- Industry
  - *Dupont ↔ Chemours*
  - *3M*
  - *3rd party manufacturers*
- Wastewater treatment plants
  - *Biosolids*
- Landfills
  - *Historic impacts*

ENVIRONMENTAL INTEREST IN PFAS

Where it began…



Perfluorooctanoic Acid
(PFOA)
≈ "Teflon®"



Perfluorooctanesulfonic Acid
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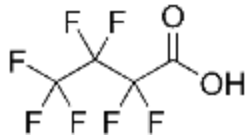
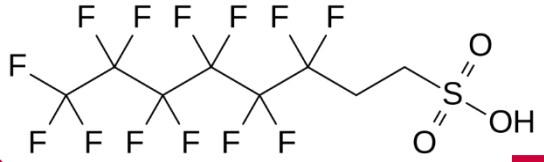


Perfluorobutanoic Acid
(PFBA)

Perfluorononanoic Acid
(PFNA)

Precursors

8:2 Fluorotelomer Alcohol
(8:2 FTOH)



6:2 Fluorotelomersulfonic Acid
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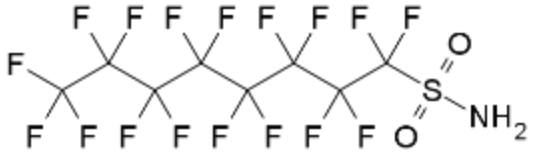

Perfluorooctanesulfonamide
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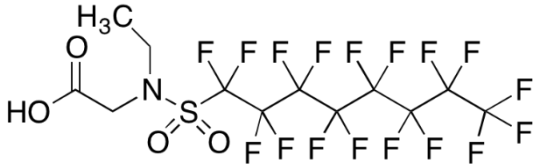
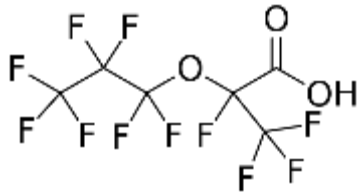
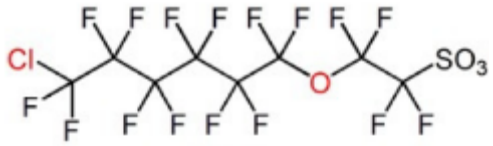


N-Ethylperfluorooctanesulfonamidoacetic Acid
(EtFOSAA)

Replacements



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



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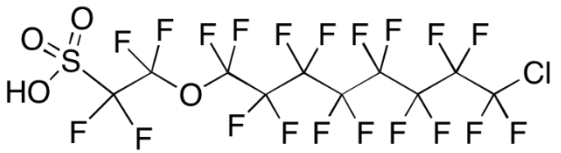
(F53B major)



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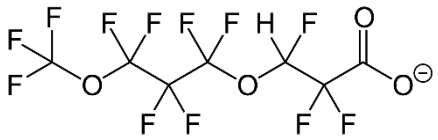


Dodecafluoro-3H-4,8-dioxanoate
(ADONA)

4000+
Compounds
("Dark Matter")

Environmental
Conversion

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 ORGANOFLUORINE ANALYSIS

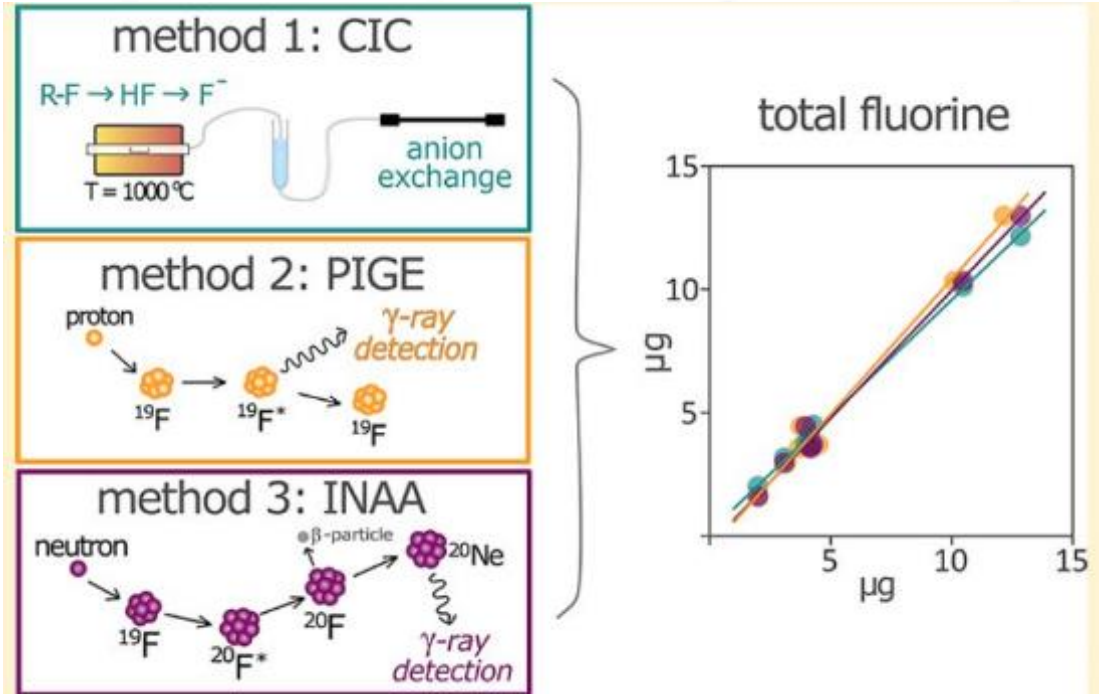
CIC: Combustion Ion Chromatography
Uses equipment similar to that in wide use in Europe for 'Adsorbable Organic Halides' (AOX) analysis.

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

ENVIRONMENTAL Science & Technology LETTERS
Letter
Cite This: Environ. Sci. Technol. Lett. 2019, 6, 73−78
pubs.acs.org/journal/estlcu

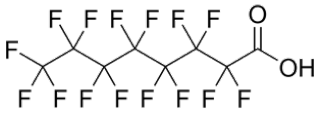
Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?



Reference: *Environ. Sci. Technol. Lett*, 2019, 6, 73-78

PFAS – BUREAU VERITAS OPTIONS

Where it began…



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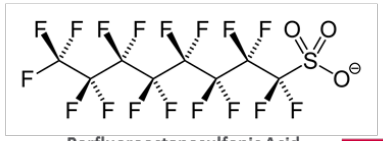

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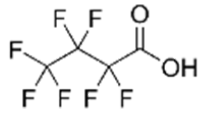

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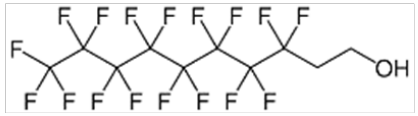

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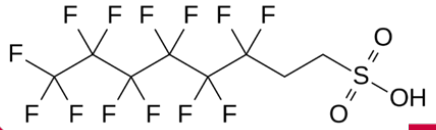

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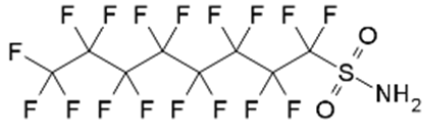

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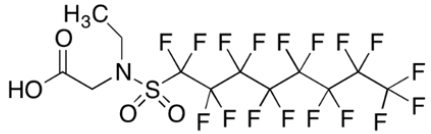

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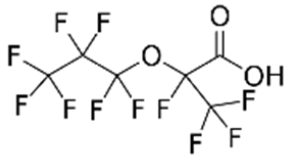

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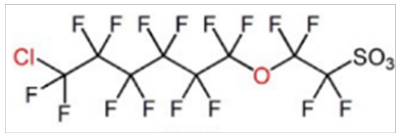

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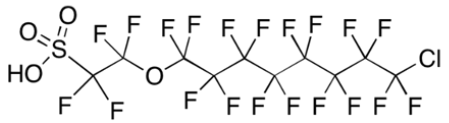

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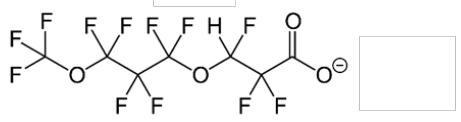


Dodecafluoro-3H-4,8-dioxanoate
(ADONA)

4000+
Compounds
("Dark Matter")

Environmental
Conversion

PFAS by LC-MS/MS

PFAS + "Dark Matter" by TOPs Assay

Total Organic Fluorine by Combustion Ion Chromatography

FIRST COMMERCIALLY VIABLE CIC-TOF METHOD

Science of the Total Environment 673 (2019) 384–391

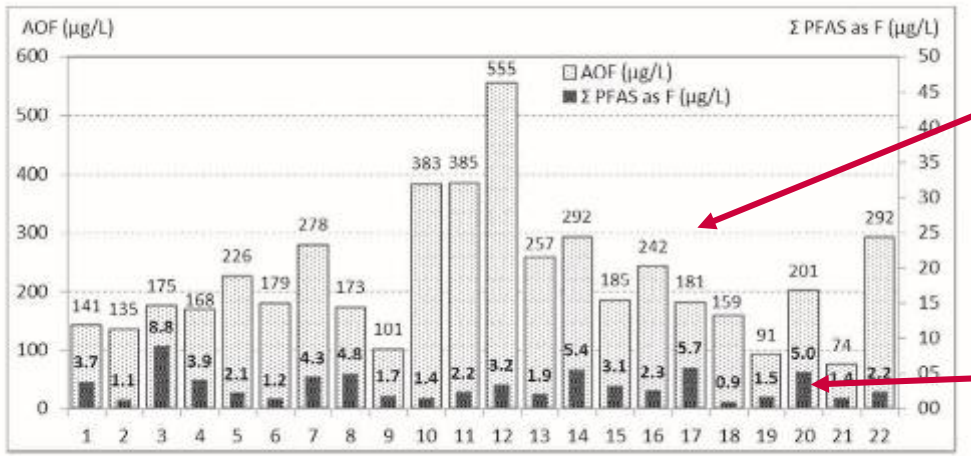
Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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



Organofluorine

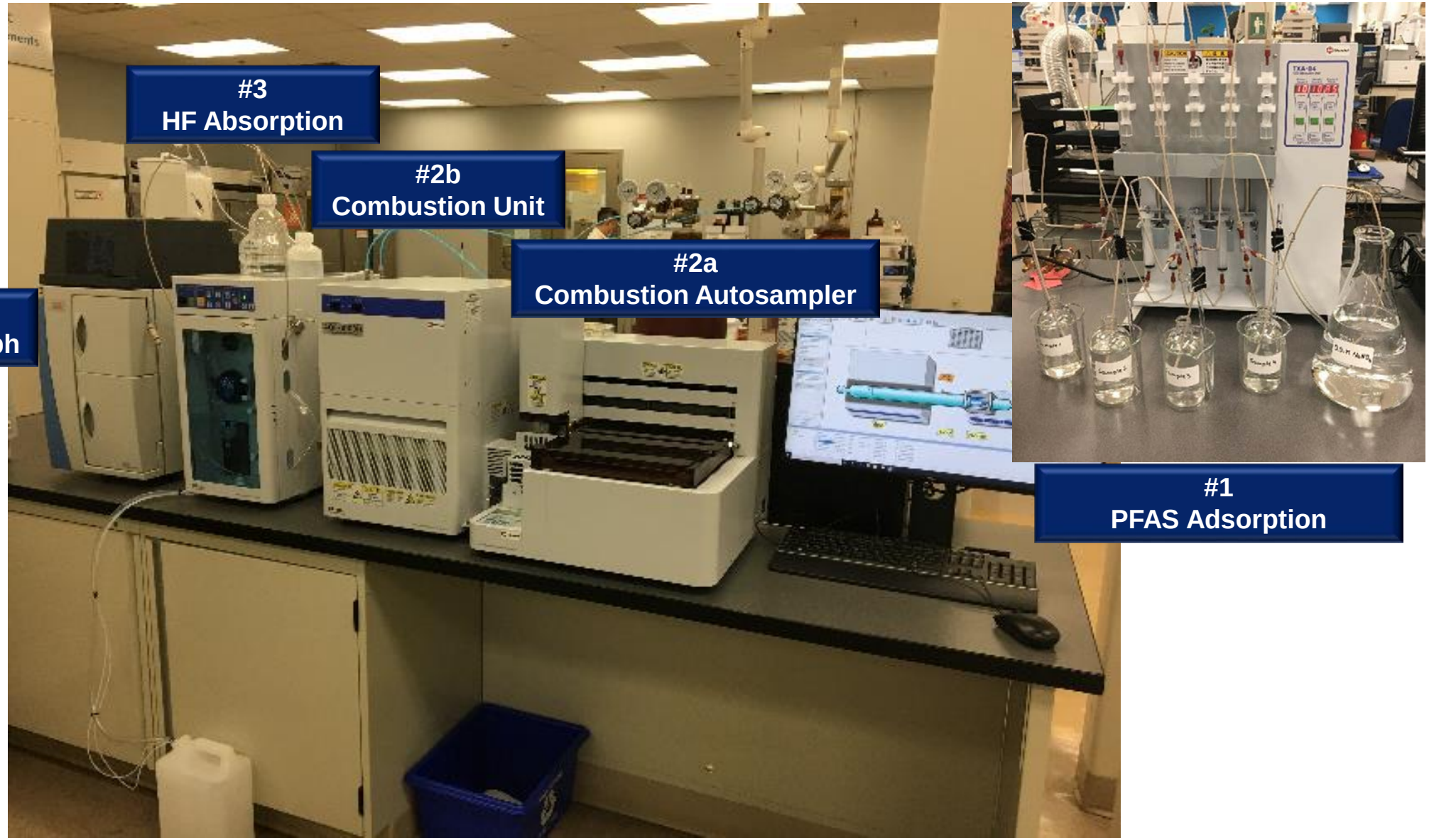
Σ PFAS (as F)

- 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

Reference: von Abercron *et.al.*: *Sci. Tot. Environ.*, 2019, 673, 384-391

BUREAU VERITAS LABORATORIES' CIC-TOF SYSTEM



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
($C_8F_{17}SO_3^-$)

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…

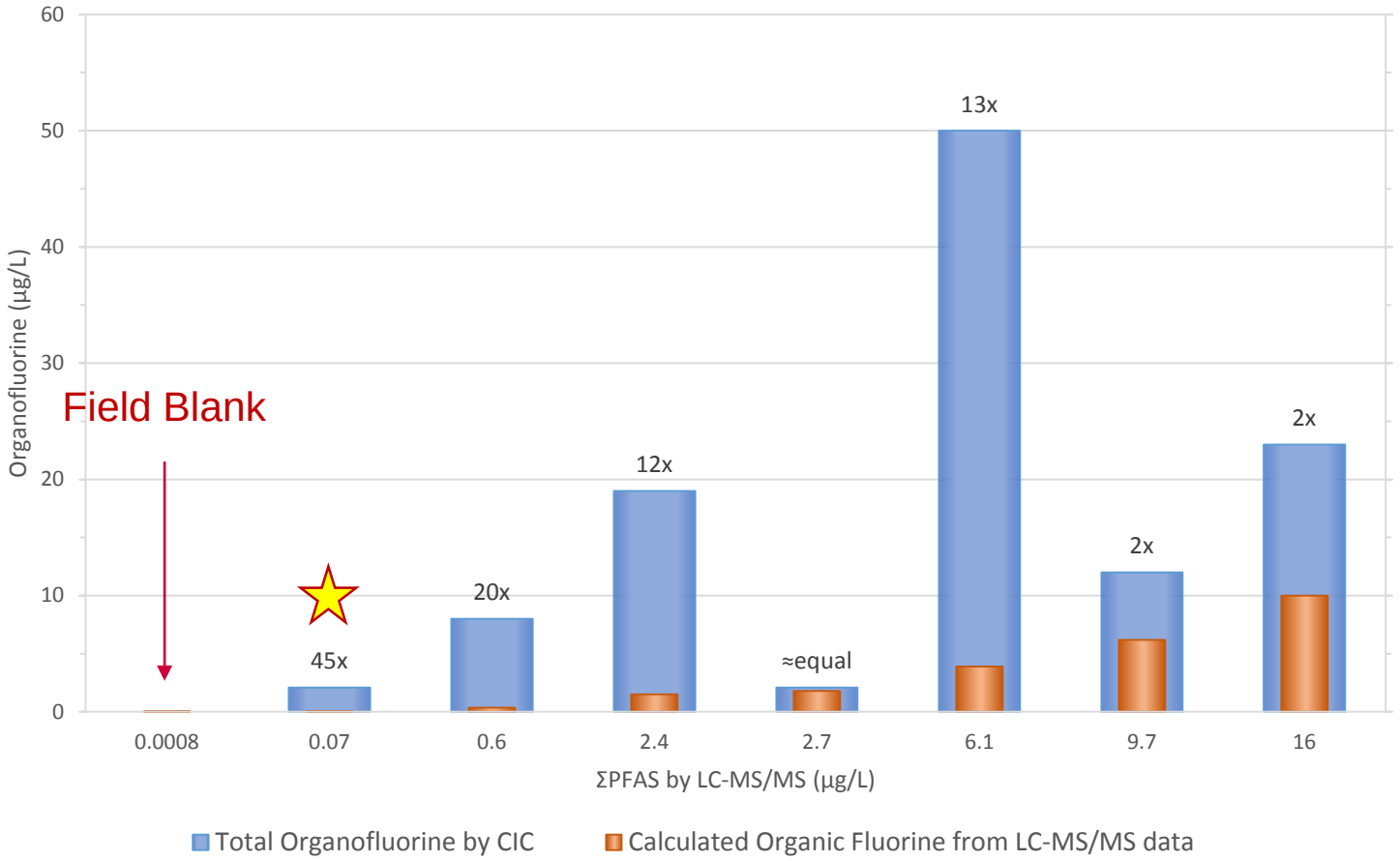
PFOS (by LC/MS/MS) = **250 ng/L PFOS**

F_{total} (by CIC) = 0.647 x 250 ng/L

= **162 ng/L F**

~65%

LC-MS/MS vs. CIC-TOF: WATER SAMPLES

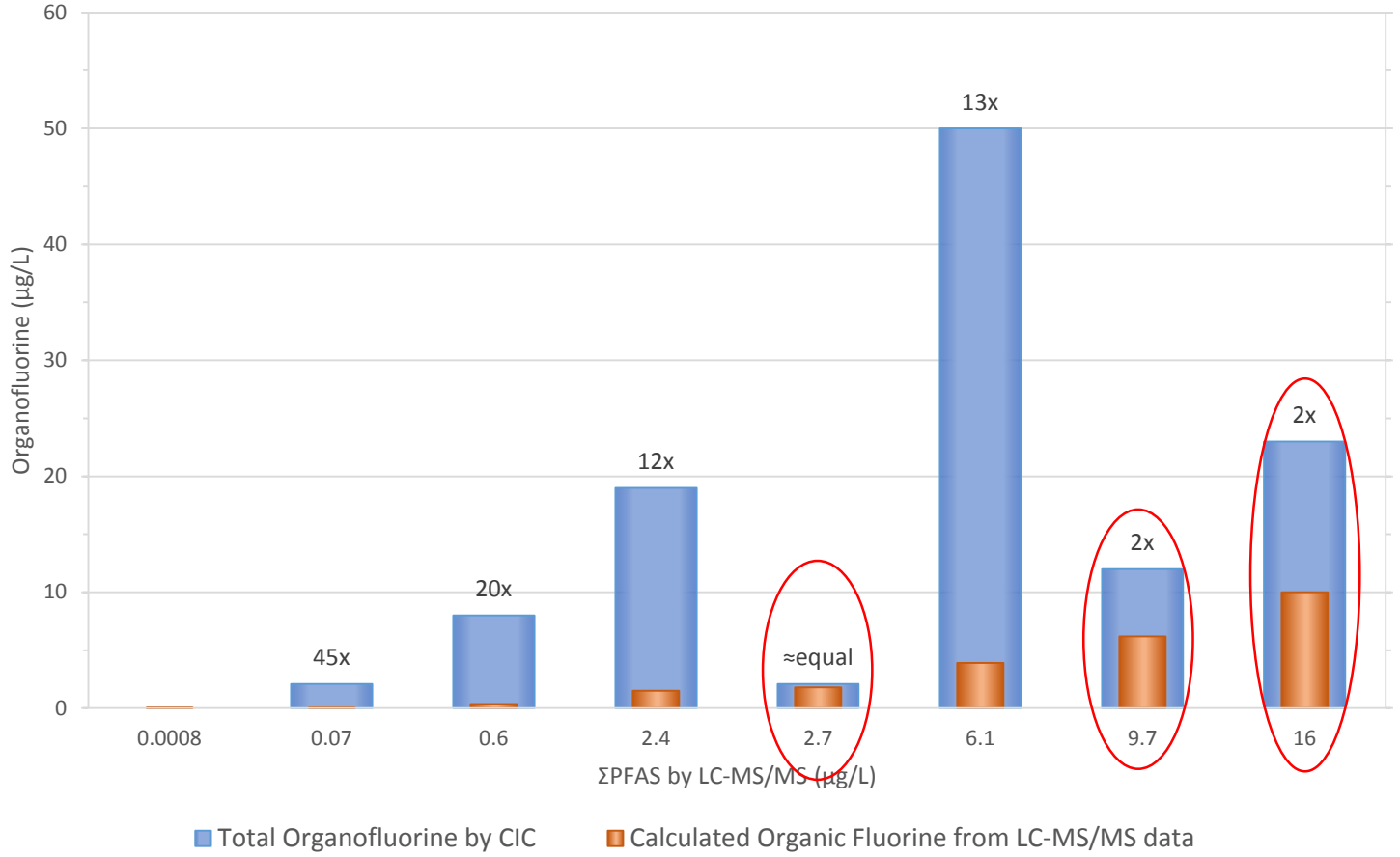


★ Sample reported by LC-MS/MS
✓ 0.07 µg/L ΣPFAS
✓ 0.002 µg/L PFOS
i.e. meets all proposed regulatory requirements.

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



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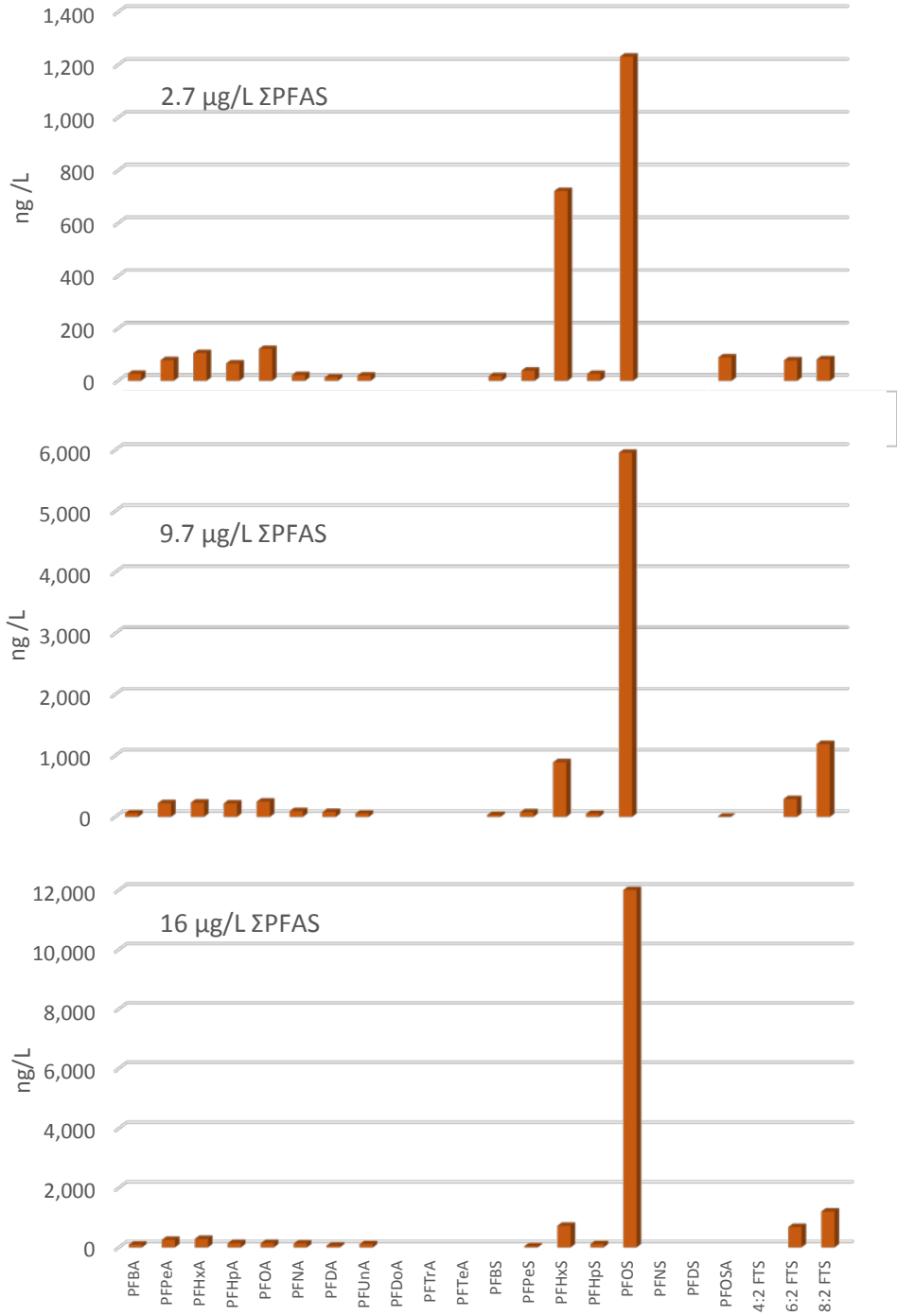
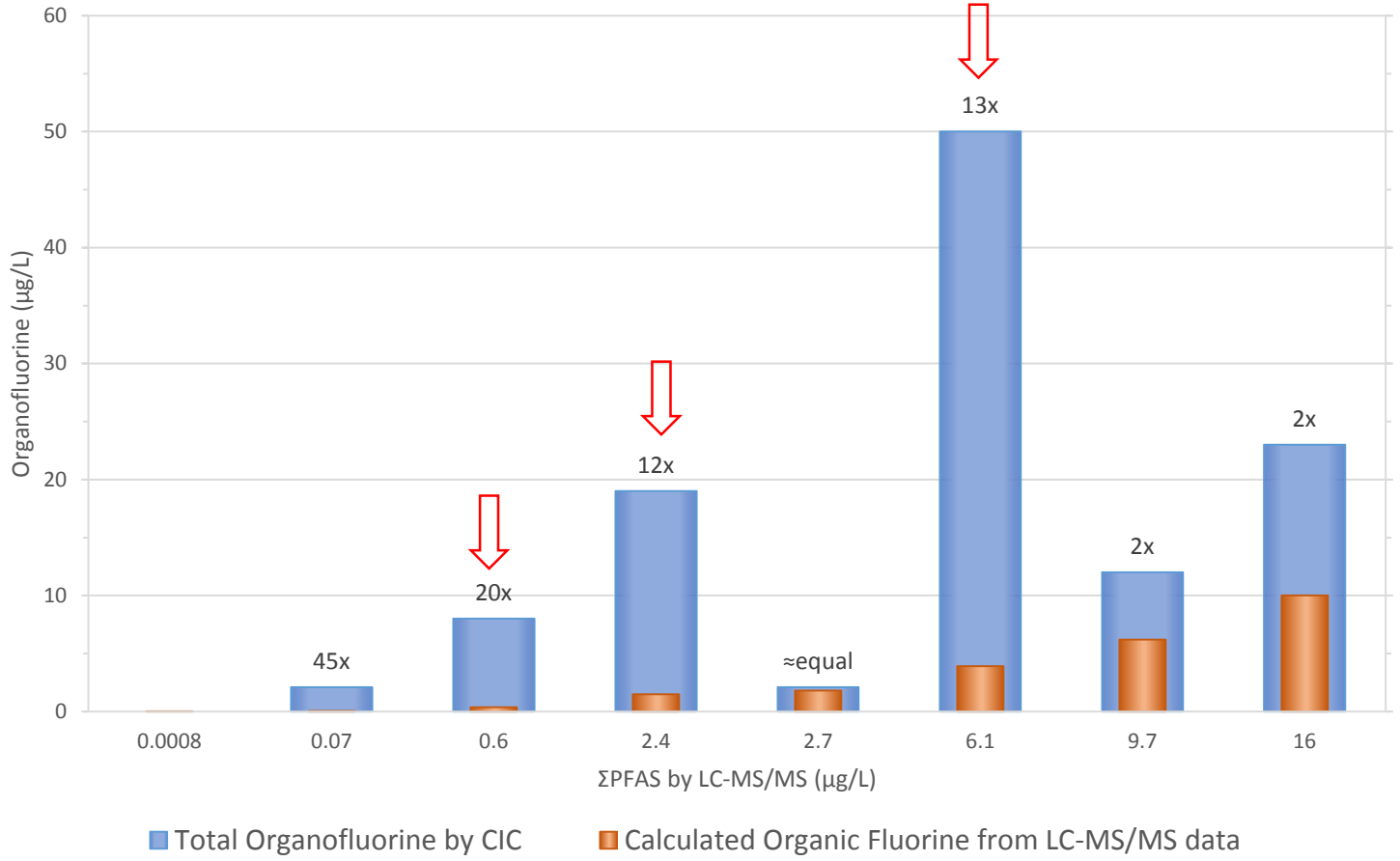


LC-MS/MS vs. CIC-TOF: WATER SAMPLES



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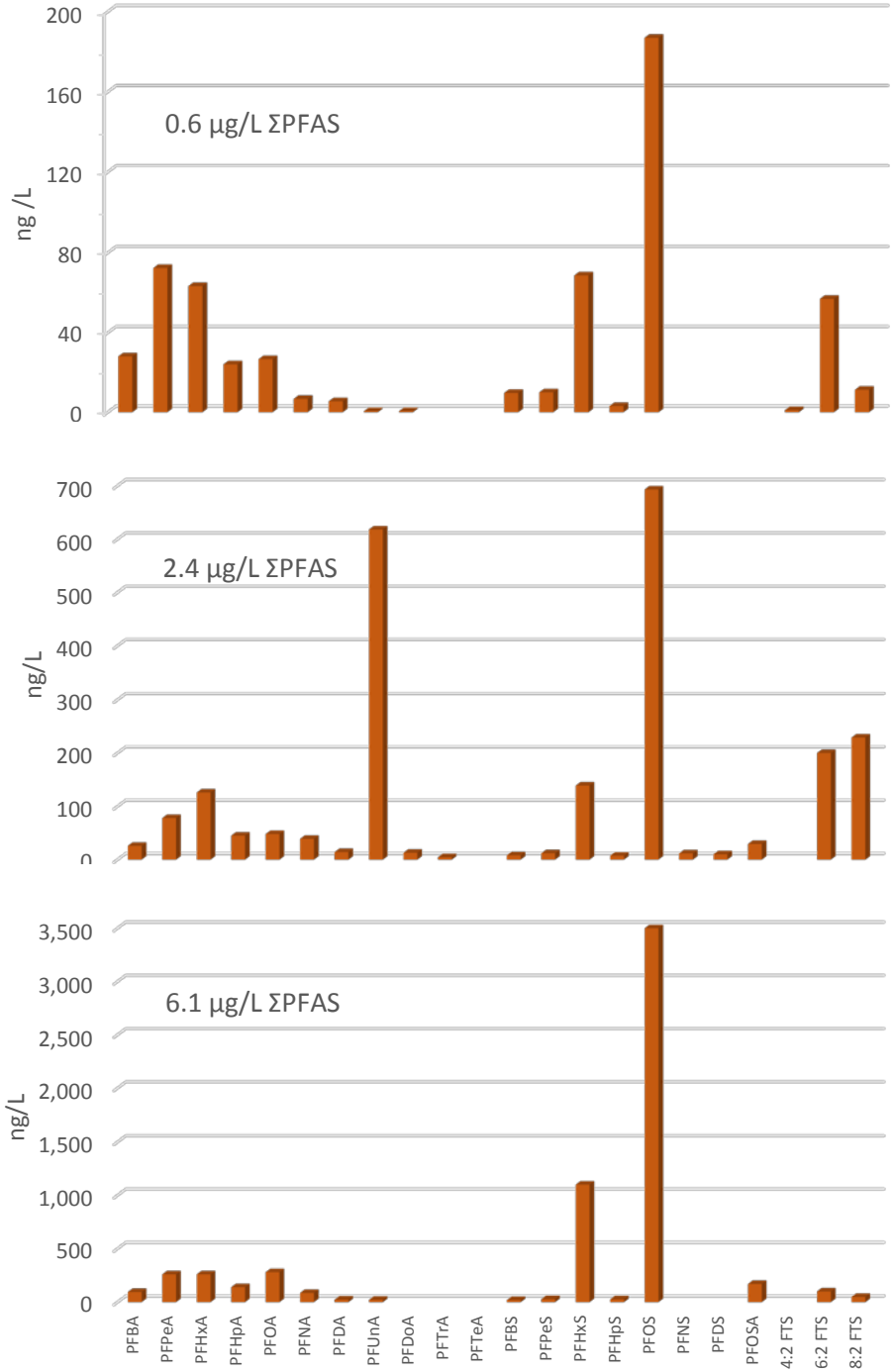
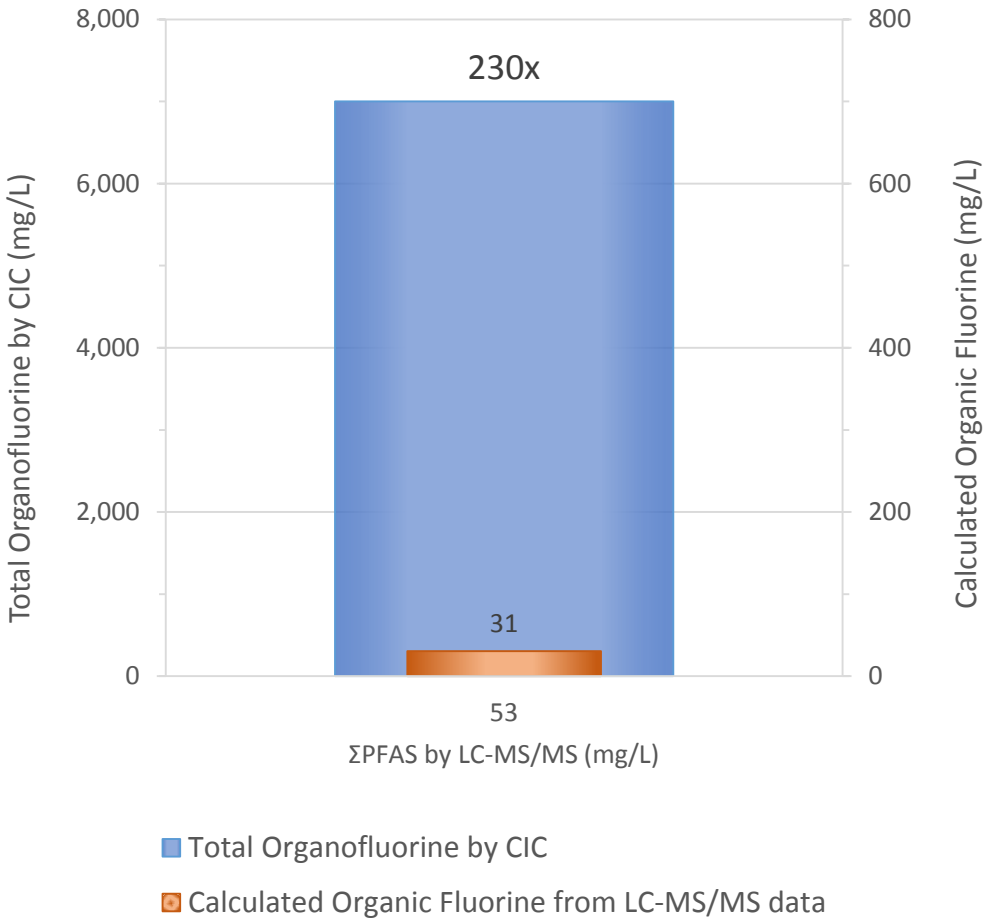
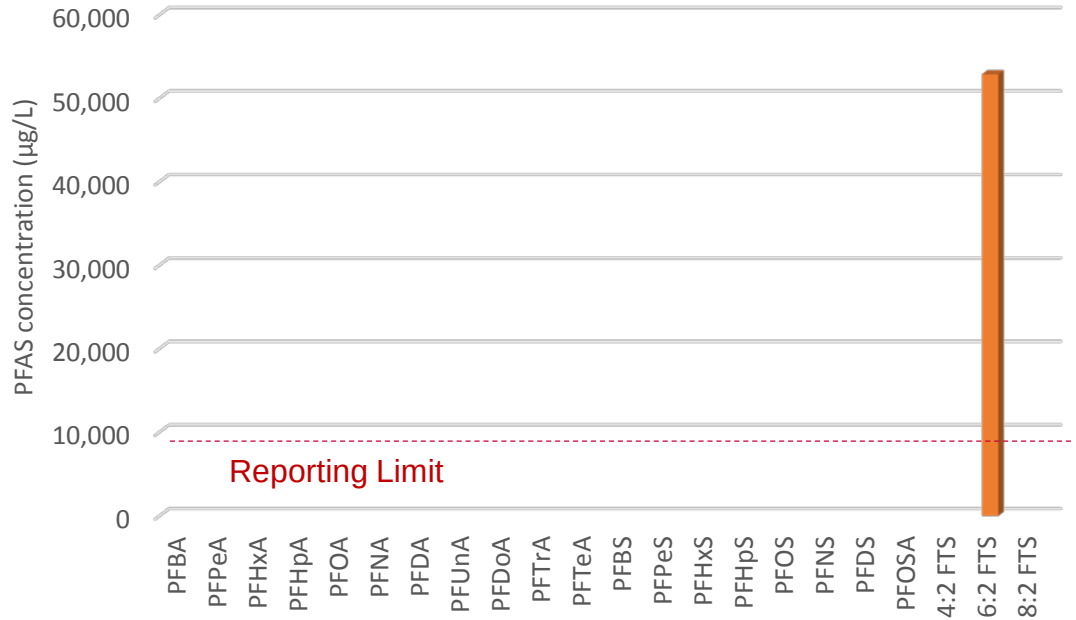


LC-MS/MS vs. CIC-TOF: AFFF SAMPLE



CIC DL: 200 mg/L (due to sample dilution)



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

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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:

Prohibited	Acceptable	Screen/Verify
• Waterproof field books • Water and dirt resistant leather gloves • Decon 90 • Chemical or “Blue” ice	• Aluminum clipboards; Loose paper • Powderless nitrile gloves • Alconox®, Liquinox® or Citrinox® • Regular ice (sealed polyethylene bags)	• Post-it Notes® • Off-brand markers • Any special gloves/clothing required as specific personal protective equipment (PPE)

BUREAU VERITAS

NEXT STEPS

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

ACKNOWLEDGEMENTS

Bureau Veritas Laboratories

Lusine Khachatryan, MSc

ThermoScientific

Peter Cheng
Kirk Chassaniol

Mandel Scientific

Ian Robinson
Ken Jespersen

COMMENTS AND QUESTIONS

Stephanie Pollen, BSc
Account Manager, Ultra Trace Analysis
stephanie.pollen@bureauveritas.com
(905) 817-5130

Heather Lord, PhD
Manager,
Environmental Research & Development
heather-lynn.lord@bureauveritas.com
(905) 817-5711

Terry Obal, PhD, CChem
Chief Science Advisor
taras.obal@bureauveritas.com
(905) 288-2174

PFAS@BVLabs.com

Shaping a World of Trust

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