Determining Total Organic Fluorine in Wastewater and Process Water Samples

2021 NEMC – Bellevue, WA

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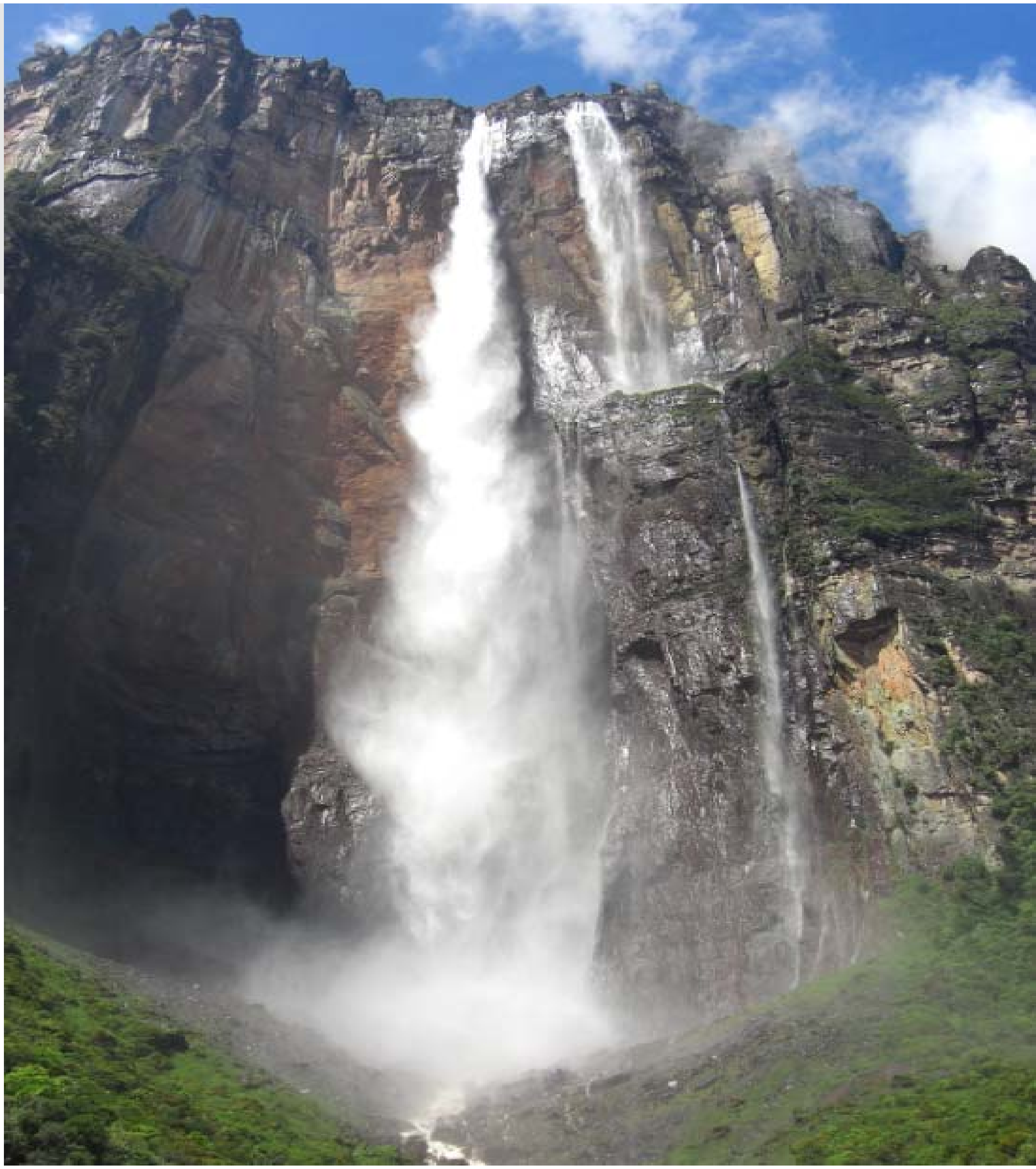
Today's Discussion

- PFAS background and trends
- Targeted vs. non-targeted analysis
- Adsorbable Organic Fluorine (AOF) sample preparation
- Combustion IC & fluorine analysis
- AOF – CIC exemplary data
- Summary

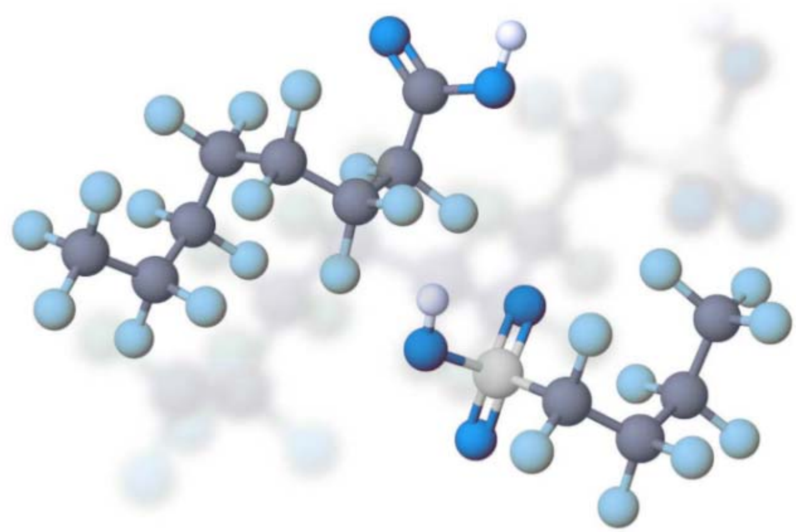


Per- and polyfluoroalkyl substances (PFAS)

PFAS are manmade “forever” chemicals used in industry and consumer products.

Exposure to PFAS may have negative health effects.

Thousands of different PFAS-related compounds have been identified.



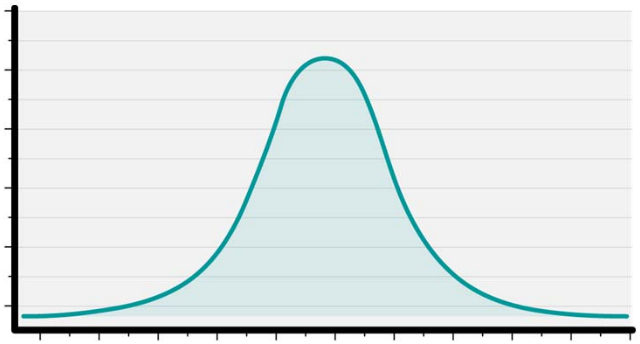
Current PFAS Regulatory Landscape

CURRENT TARGETED METHODS FOR LC-MS/MS:

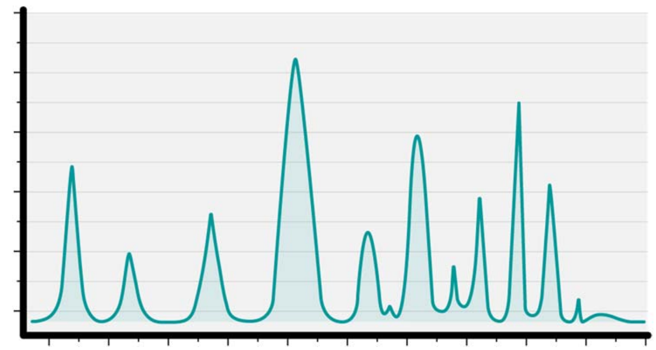
- **USEPA 533**
- **USEPA 537.1**
- **ASTM D7979**
- **SW846 method 8327**

LC-MS/MS Targeted Technique

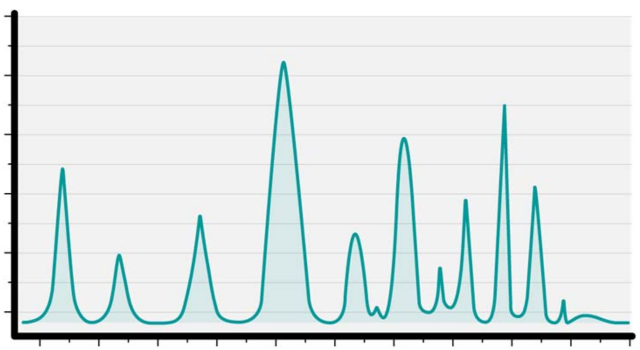
Separate sample into known PFAS compounds



Chromatography



Use of expensive standards to quantify short list of compounds by MS



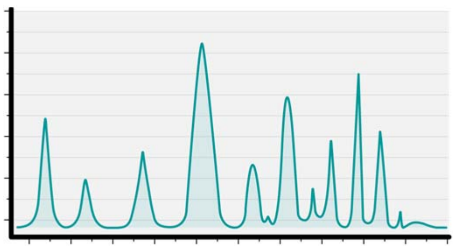
Quantify

Analyte	Recovery
PFBS	…
PFHxS	…
PFOS	…
PFBA	…
PFOA	…
PFNA	…

Cons of Targeted LC-MS/MS

Identifies only a small fraction of Total PFAS

Quantifies an even smaller fraction of PFAS compounds with MS standards



Analyte	Recovery
PFBS	...
PFHxS	...
PFOS	...
PFBA	...
PFOA	...
PFNA	...

≠ Total Impact

Does not determine the organic fluoride, the indicator of overall impact

Approaches to Measuring PFAS

Targeted analysis:

- Measure selected PFAS compounds using specific methodologies
- Currently limited to < 100 compounds
- Common technique: LC-MS/MS

Non-targeted analysis:

- Better risk assessment tool for true "impact" in the environment
- Measure organic fluorine
- Emerging technique: Combustion IC w/ AOF

Non-Targeted Analysis of Organic F with CIC

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HOT TOPIC

Direct Combustion

Direct combustion:

Combustion of sample in CIC to measure Total F in solids/liquids

- **Sample Prep**
  - No Sample Prep
- Approx. detection limit: 50 ppb F

Extractable Org F (EOF)

Capture & Elute:

Combustion of extracted liquid sample in CIC to measure Org F

- **Sample Prep**
  - Sample is passed through anion exchange cartridge
  - Elute PFAS with methanol & concentrate
- Approx. detection limit: 0.5-2 ppb (Sx Prep Dependent)

USEPA Method 533/537 or some modified version of

Adsorbable Org. F (AOF)

Capture & Combust:

Adsorption of Sample on to GAC and combust in CIC to measure Org F

- **Sample Prep**
  - Sample is passed through activated charcoal bed
  - Final wash with nitrate solution to remove inorganic fluoride
- Approx. detection limit: 0.5-2 ppb (Sx Prep Dependent)

Proposed method for ASTM/USEPA/DIN/ISO

AOF with Combustion IC

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Profiler F
TOTAL FLUORINE ANALYZER

Most widely accepted technique available for non-targeted analysis with emerging regulatory landscape:

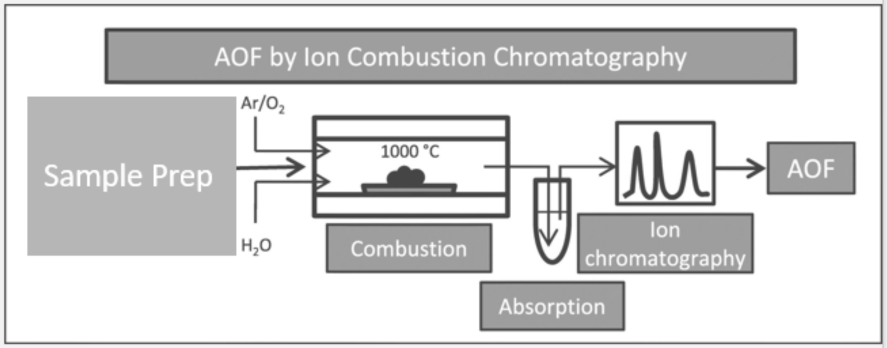
ASTM WK 68866:

- New Test Method for Determination of Adsorbable Organic Fluorine in Waters and Waste Waters by adsorption on Activated Carbon followed by Combustion Ion Chromatography

DIN 38409-59:

- **Determination of adsorbable organically bound fluorine**, *chlorine, bromine and iodine* (**AOF**, AOCl, AOBr, AOI) after combustion and ion chromatographic measurement
- Interlaboratory ruggedness study in progress

Commonly referred to as "Capture and Combust"



- Extracting up to 100mL sample provides improved detection (100X less than by direct CIC measurement)
- Complementary to LC-MS/MS methods as screening tool

Adsorbable Organic Fluorine (AOF)

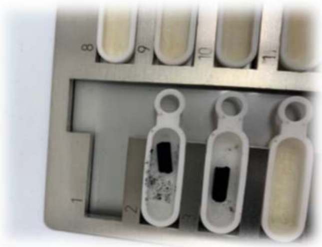
HOW DOES IT WORK?

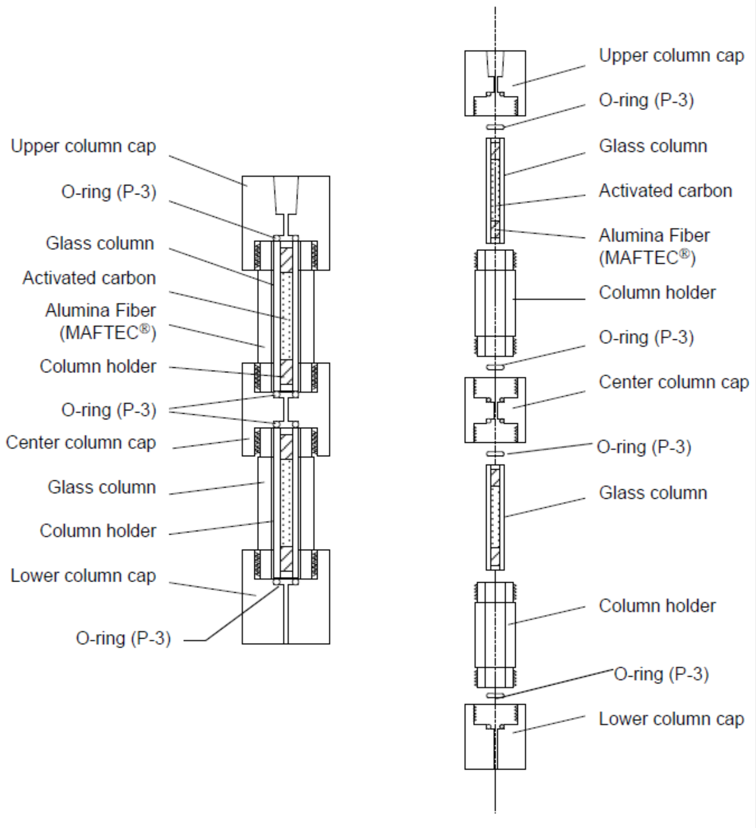
Pass 100mL of liquid sample through activated carbon (organic compounds will stick to carbon)

Wash it with 25mL 10mM $NaNO_3$ to remove free fluoride

Nitrate Wash

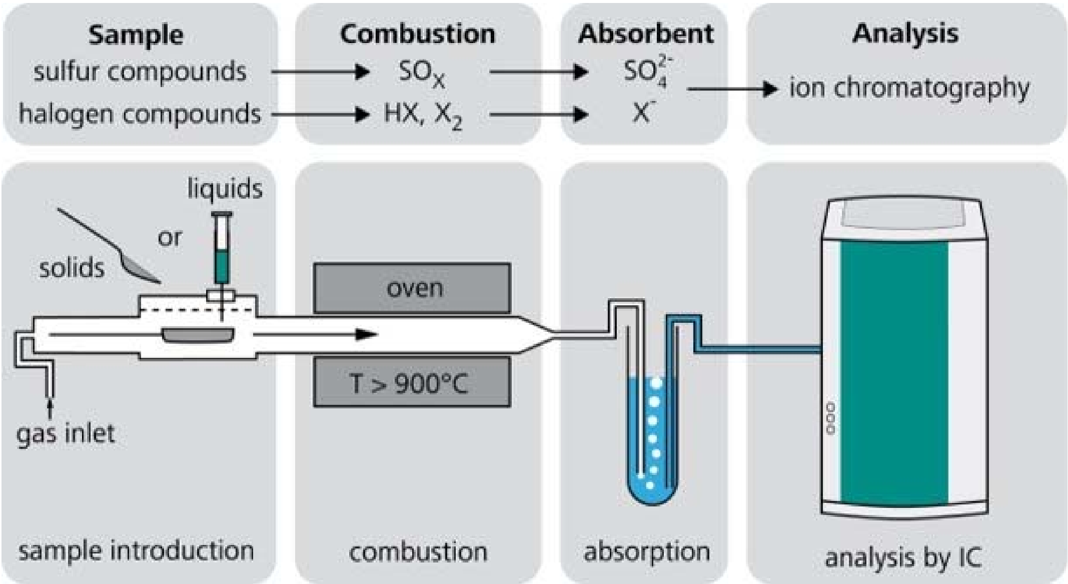
Analyze carbon of each tube by Combustion IC





Combustion Ion Chromatography

HOW DOES IT WORK?



Charcoal from each extracted tube is placed in a sample boat → Sample is combusted at 1050°C in oxygen and water to break C-F bond → Fluoride is trapped in absorber solution → Absorber solution is analyzed by IC for F^-

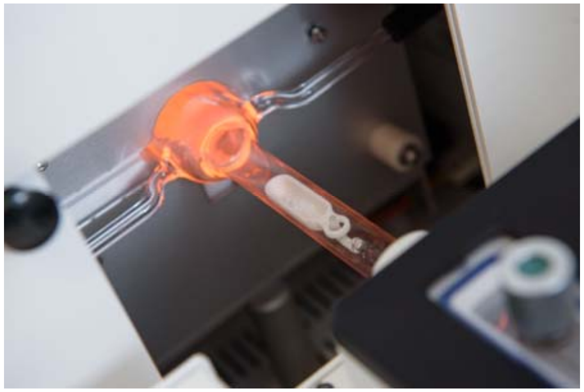
Combustion Ion Chromatography with AOF

Fully-automated measurement of Fluorine

Configured for AOF samples:

- Solids (Extracted charcoal)
- Liquids (standards, extracts, QC)

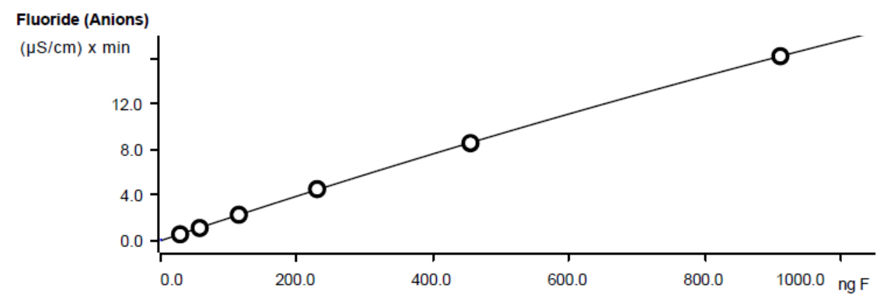
Flexible Calibration options



Calibration Options:

IC Calibration (only IC)

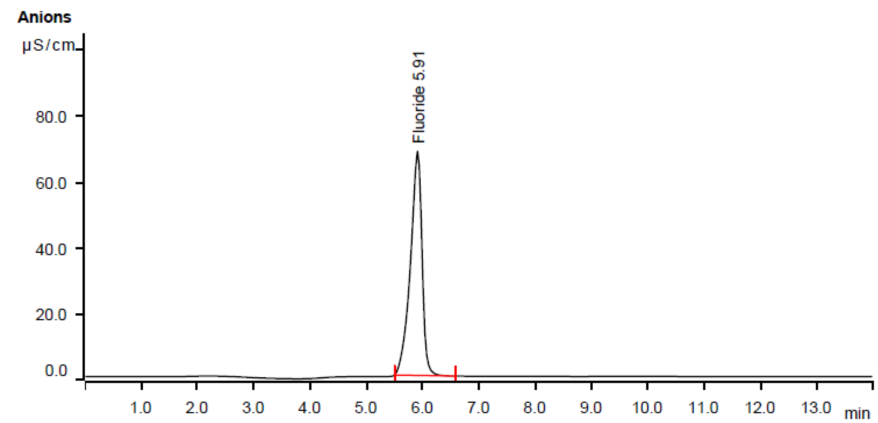
1) **Calibrate IC** using a series of inorganic fluoride standards (*mass F* vs. *instrument response*)
2) **IC Recovery Check:** Analyze IC check standard to verify recovery
3) **CIC Recovery Check:** Analyze an organic fluoride check standard through the entire combustion system to verify recovery of organic fluoride in CIC (**Note:** *What happens when CIC recovery stays at 80% ?)*
4) **AOF – CIC Recovery Check:** Extract PFAS from a known aqueous sample containing organic fluoride by AOF and analyze charcoal by CIC to verify recovery of organic fluoride through the entire AOF – CIC process



Function: . . . . $A = -0.0524388 + 2.11477E\text{-}5 \times Q - 2.72938E\text{-}12 \times Q^2$

Relative standard deviation . . . . 0.837092 %

Correlation coefficient 0.999982



Calibration Options:

IC Calibration (only IC)

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2) **IC Recovery Check:** Analyze IC check standard to verify recovery
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   NOTE: *WHAT HAPPENS WHEN CIC RECOVERY STAYS AT 80% ?*

4) **AOF – CIC Recovery Check:** Extract PFAS from a known aqueous sample containing organic fluoride by AOF and analyze charcoal by CIC to verify recovery of organic fluoride through the entire AOF – CIC process

Calibration Options:

Calibration through Furnace (full CIC calibration)

1) **Calibrate CIC** using a series of organic fluoride standards (*mass F* vs. *instrument response*)
2) **CIC Recovery Check:** Analyze an organic fluoride check standard through the entire combustion system to verify recovery of organic fluoride in CIC

   NOTE: *IT DOESN'T MATTER IF RECOVERY IS ALWAYS 80%.*

3) **AOF – CIC Recovery Check:** Extract PFAS from a known aqueous sample containing organic fluoride by AOF and analyze charcoal by CIC to verify recovery of organic fluoride through the entire AOF – CIC process

AOF – CIC: Exemplary Data

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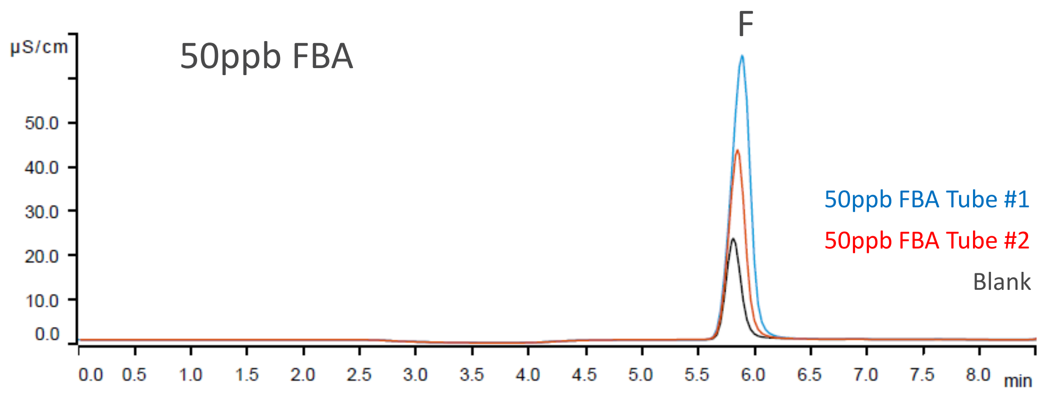
Demonstrate recovery of a known standard across a range of concentrations

- Stock: 1ppm as F using 4-Fluorobenzoic acid in ethanol
- Evaluation Standards: 5, 10, 50, 100ppb F



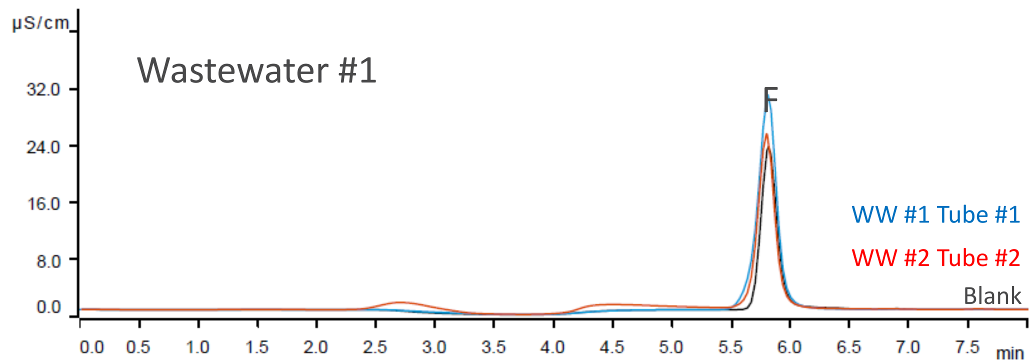
Sample ID	Total Peak Area (µS/cm x min)	Total Mass F (ng) on-column	Concentration (µg/L, ppb)	% RSD	Recovery
Blank	3.20	157	10.98	5.9	-
5ppb FBA	4.99	221	**6.68***	8.9	134%
10ppb FBA	6.36	316	**11.16***	12.0	112%
50ppb FBA	20.05	1026	**49.85***	6.4	100%
100ppb FBA	28.63	1523	**84.65***	5.3	85%

Total Peak Area, Total Mass F = sum of 2 tubes in series per sample
* Blank subtracted values

AOF – CIC: Exemplary Data

Unknown Samples: Ruggedness Study

- Standard sample
- Surface water sample
- Wastewater sample #1
- Wastewater sample #2



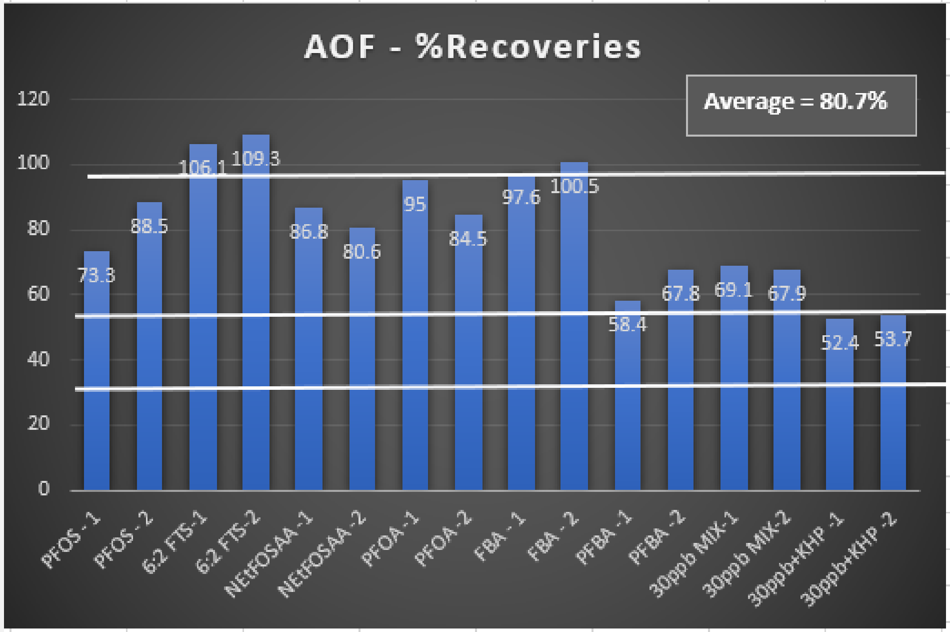
Sample ID	Total Peak Area (µS/cm x min)	Total Mass F (ng) on-column	Concentration (µg/L, ppb)	% RSD
Blank	3.20	157	10.98	5.9
Standard	4.57	237	**6.48***	0.9
Surface water	4.62	240	**6.68***	4.1
Wastewater 1	9.82	510	**15.65***	6.6
Wastewater 2	4.29	222	**6.17***	7.6

N = 4 samples
Total Peak Area, Total Mass F = sum of 2 tubes in series per sample
* Blank subtracted values

AOF Data – Independent Evaluation
50mls Sample used for AOF

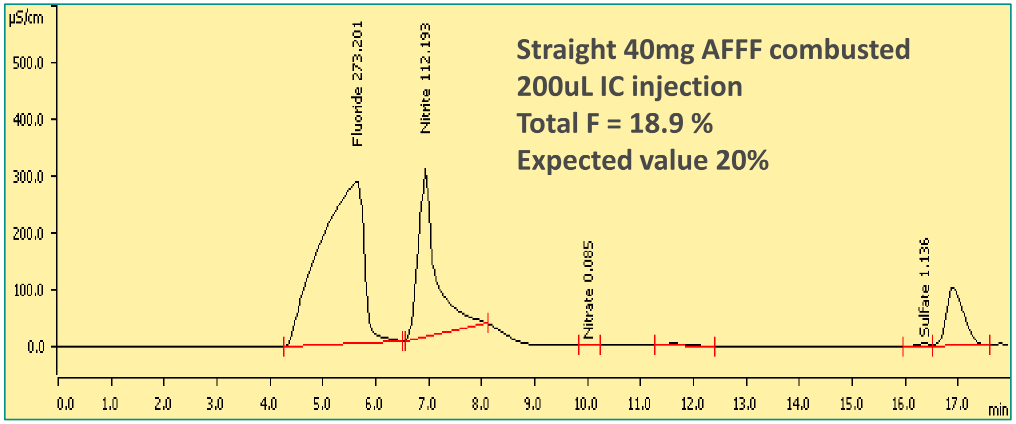
Courtesy : Dr. Charles Neslund, Eurofins Labs

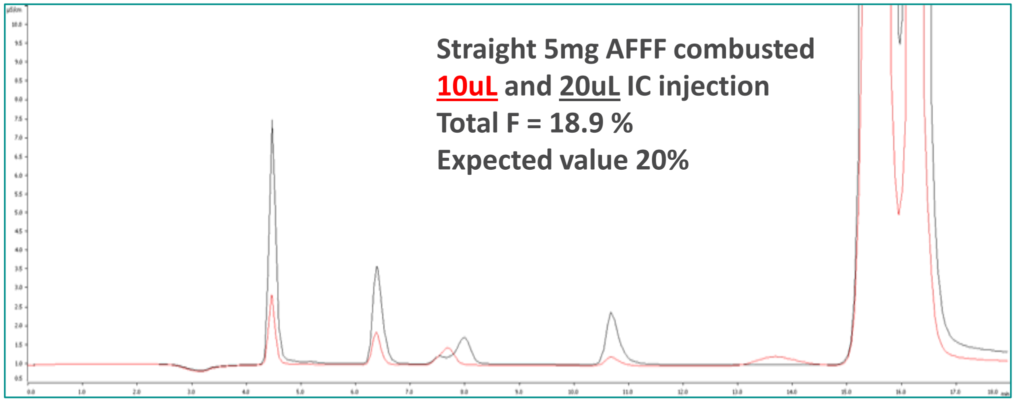
Sample ID	% recovery, AOF
PFOS - 1	73.3
PFOS - 2	88.5
6:2 FTS-1	106.1
6:2 FTS-2	109.3
NEtFOSAA -1	86.8
NEtFOSAA -2	80.6
PFOA -1	95
PFOA -2	84.5
FBA - 1	97.6
FBA - 2	100.5
PFBA -1	58.4
PFBA -2	67.8
30ppb MIX-1	69.1
30ppb MIX-2	67.9
30ppb+KHP -1	52.4
30ppb+KHP -2	53.7
Average	**80.7**

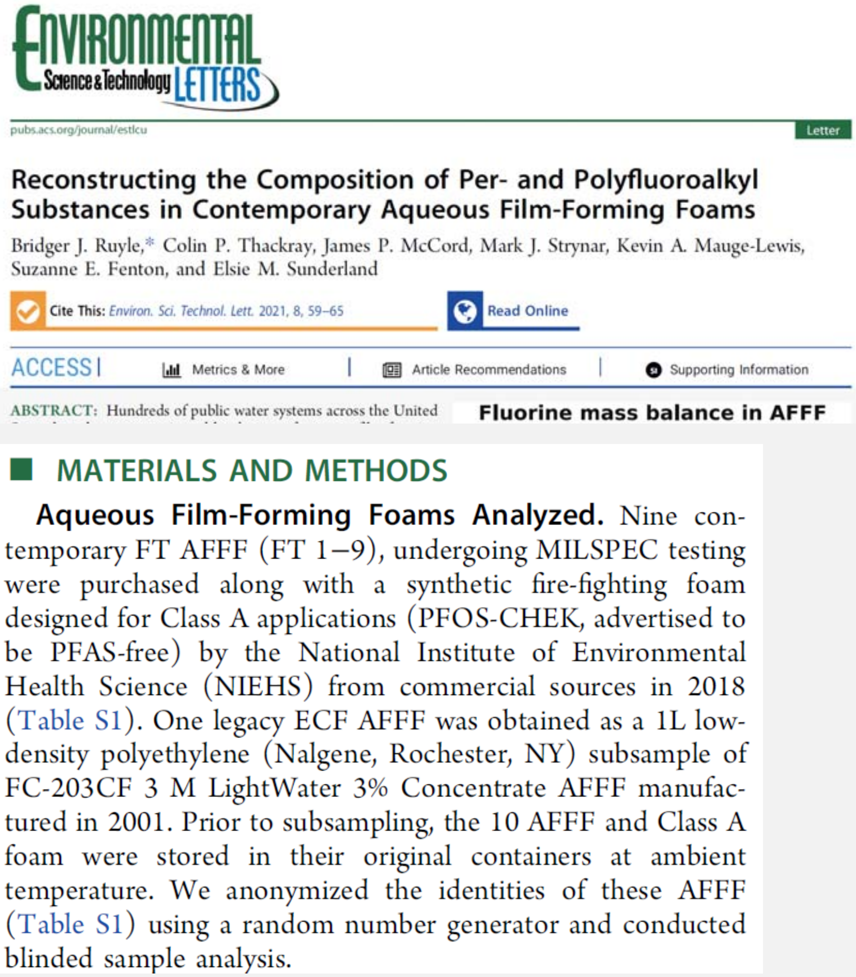


Note: When High TOC value samples were subjected to 6 carbon beds in series, PFAS recovery is ~79%

AFFF samples







Environmental Science & Technology LETTERS

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Reconstructing the Composition of Per- and Polyfluoroalkyl Substances in Contemporary Aqueous Film-Forming Foams

Bridger J. Ruyle,* Colin P. Thackray, James P. McCord, Mark J. Strynar, Kevin A. Mauge-Lewis, Suzanne E. Fenton, and Elsie M. Sunderland

Cite This: *Environ. Sci. Technol. Lett.* 2021, 8, 59−65 Read Online

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ABSTRACT: Hundreds of public water systems across the United

Fluorine mass balance in AFFF

MATERIALS AND METHODS

Aqueous Film-Forming Foams Analyzed. Nine contemporary FT AFFF (FT 1−9), undergoing MILSPEC testing were purchased along with a synthetic fire-fighting foam designed for Class A applications (PFOS-CHEK, advertised to be PFAS-free) by the National Institute of Environmental Health Science (NIEHS) from commercial sources in 2018 (Table S1). One legacy ECF AFFF was obtained as a 1L low-density polyethylene (Nalgene, Rochester, NY) subsample of FC-203CF 3 M LightWater 3% Concentrate AFFF manufactured in 2001. Prior to subsampling, the 10 AFFF and Class A foam were stored in their original containers at ambient temperature. We anonymized the identities of these AFFF (Table S1) using a random number generator and conducted blinded sample analysis.

Importance of low background

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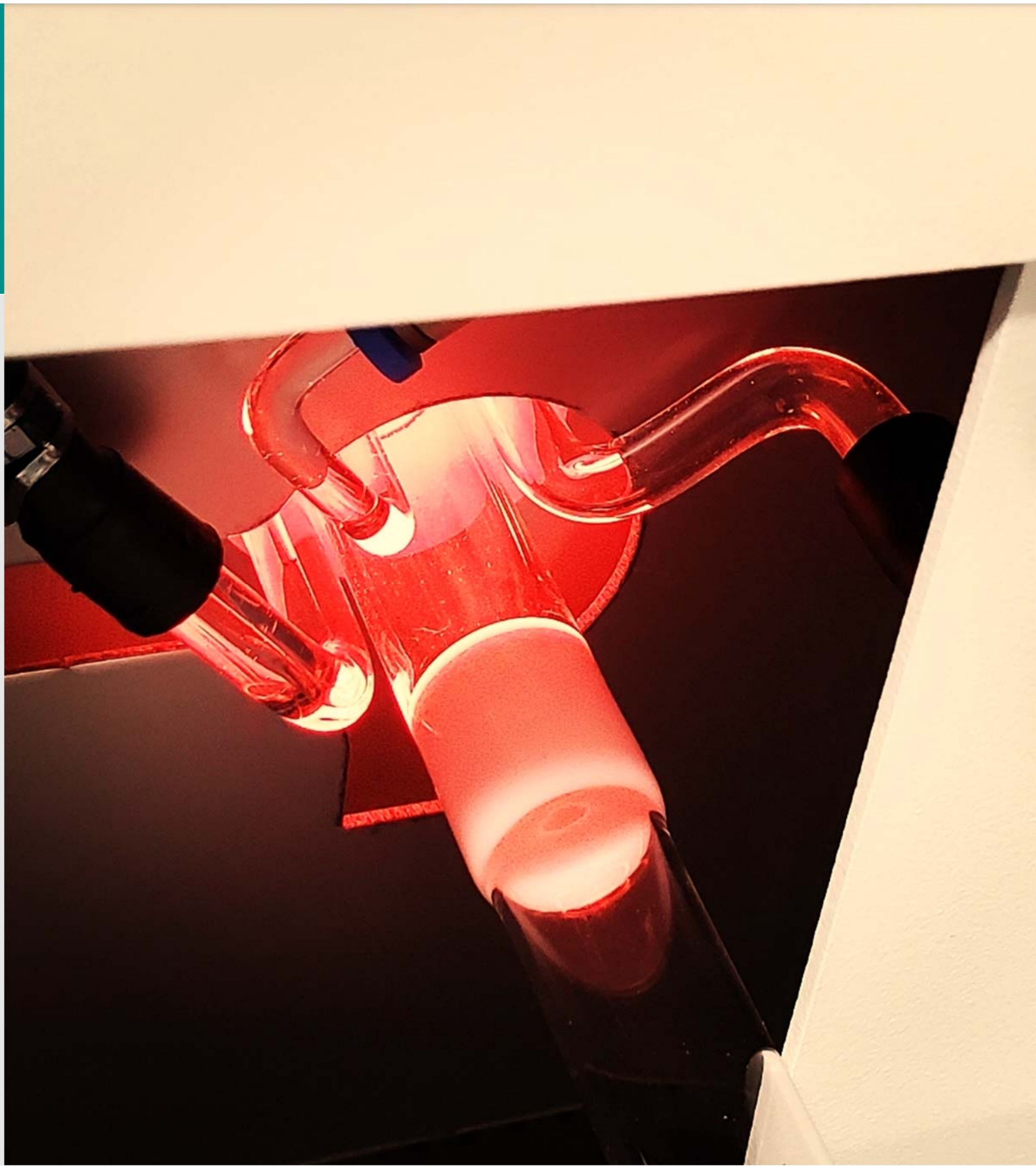
In the AOF – CIC technique, there are several places where background contribution can adversely affect results and sensitivity. *Minimizing the blank values are key.*

The keys to success…

- Use suitable activated charcoal tubes **(AOX vs AOF)**
- Use high purity water/reagents
- Proper operation of the Combustion IC system to control background contribution
- Good laboratory practice

Summary

- Non-targeted analysis provides a better risk assessment of true PFAS impact
- Organic fluoride measurements capture more information than targeted PFAS analysis alone
- Combustion ion chromatography is ideal for measuring total fluorine in a variety of sample types
- Adsorbable Organic Fluoride sample preparation effectively removes inorganic fluoride and concentrates organic fluoride compounds
- Accrediting bodies are actively developing AOF-CIC testing methodologies



Metrohm CIC Advantage

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Profiler F
TOTAL FLUORINE ANALYZER

1. Robust & Efficient Combustion
2. Low Cost of Operation
3. Flexible Calibration Options
4. One Software Platform
5. All-inclusive Support of Complete Combustion IC System

Thank You

Questions? Please contact us at communications@metrohmusa.com