Determining Total Organic Fluorine in Wastewater and Process Water Samples

2022 NEMC – Crystal City, VA

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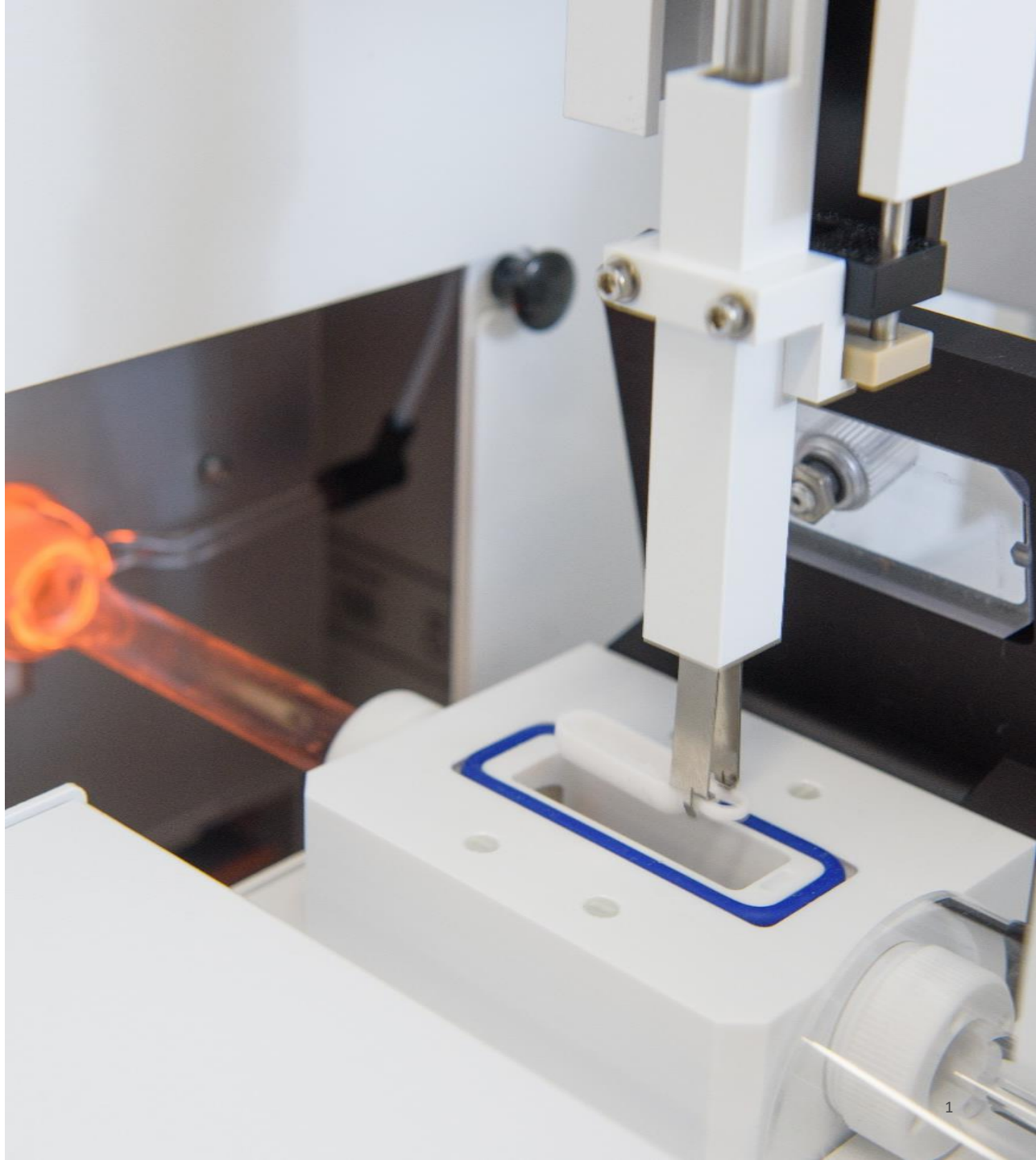
Metrohm USA



Today's Discussion

- PFAS background and trends
- Targeted vs. non-targeted analysis
- Water, Wastewater Analysis
  - Adsorbable Organic Fluorine (AOF)
  - Extractable Organic Fluoride (EOF)
  - Direct Inject - CIC
- Combustion IC & fluorine analysis
- Exemplary data with Profiler-F
- Summary

Per- and polyfluoroalkyl substances (PFAS)

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

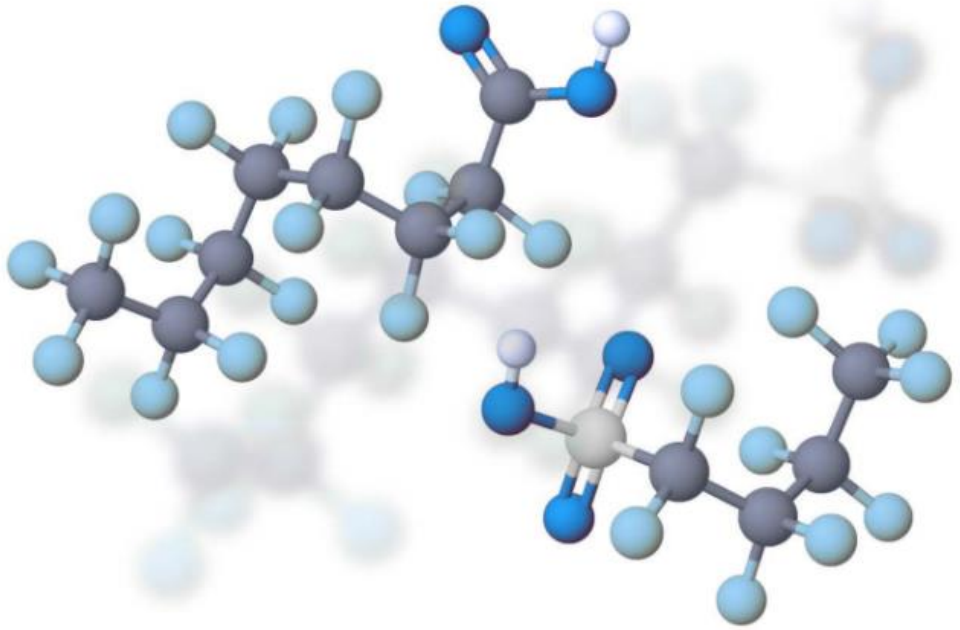
Exposure to PFAS may have negative health effects.

Thousands of different PFAS-related compounds have been identified.

Nonstick Cookware

Water-Repellant Clothing

Firefighting Foams



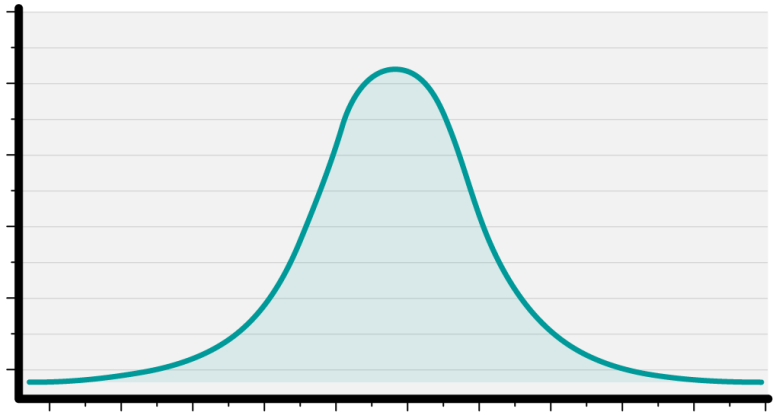
Current PFAS Regulatory Landscape

CURRENT TARGETED METHODS FOR LC-MS/MS:

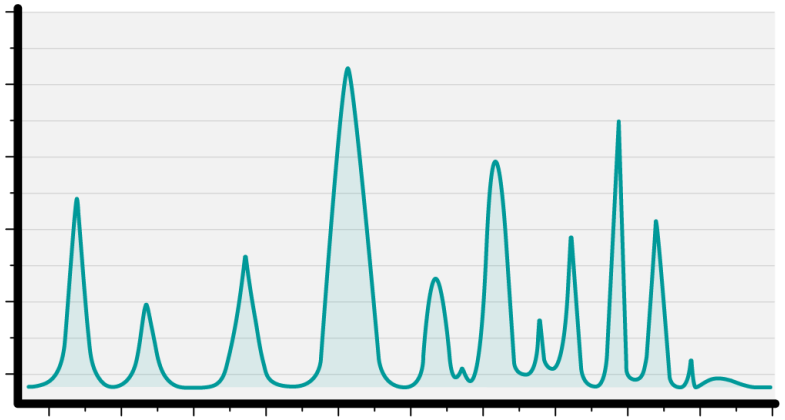
- **USEPA 533**
- **USEPA 537.1**
- **ASTM D7979**
- **SW846 method 8327**

LC-MS/MS Targeted Technique

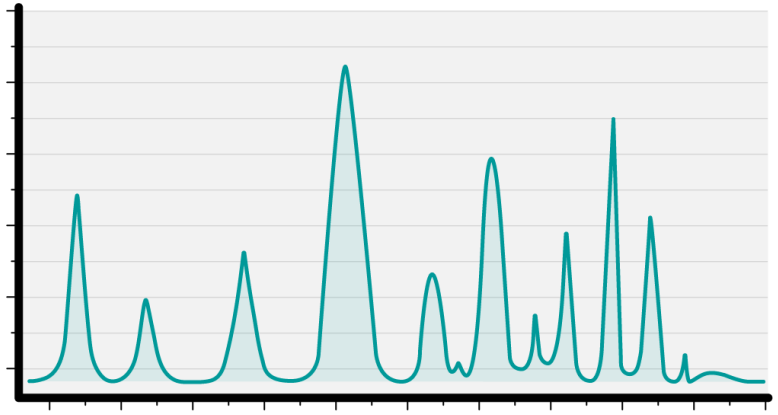
Separate sample into known PFAS compounds



Chromatography



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



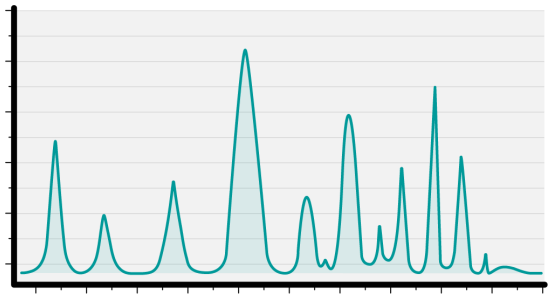
Quantify

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

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)

USEPA Draft Method 1621
DIN 38409-59

Profiler F
TOTAL FLUORINE ANALYZER

Metrohm

Confidential

Solids Sample configuration

Solids Sample Configuration (AOF/EOF)

- ✓ Robust Combustion efficiency
- ✓ Improved condenser tube
- ✓ More flexibility of large volume sample injection into IC
- ✓ Ability to achieve lower calibration ranges

AOF with Combustion IC

USEPA Draft method 1621

Metrohm

Profiler F
TOTAL FLUORINE ANALYZER

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

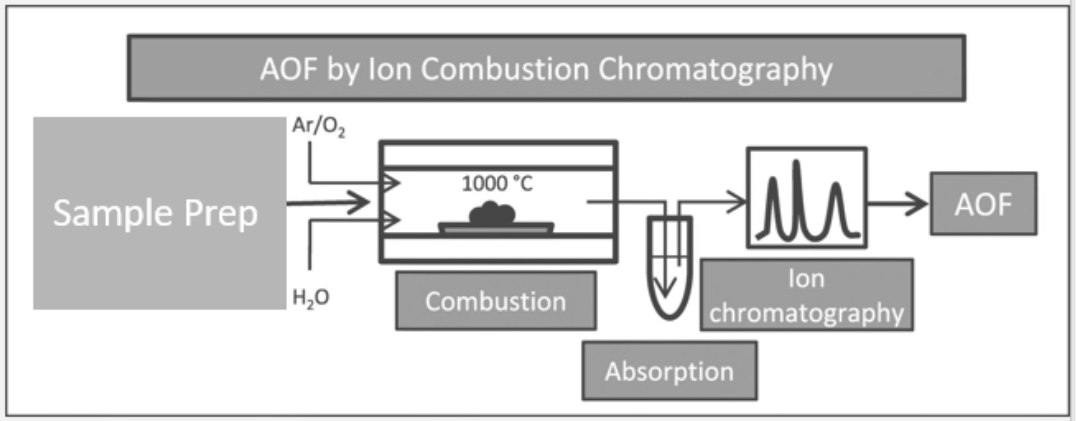
ASTM WK 68866: (Collaborative work with USEPA)

- 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: (Final method to be released in 2022)

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

Commonly referred to as "Capture and Combust"

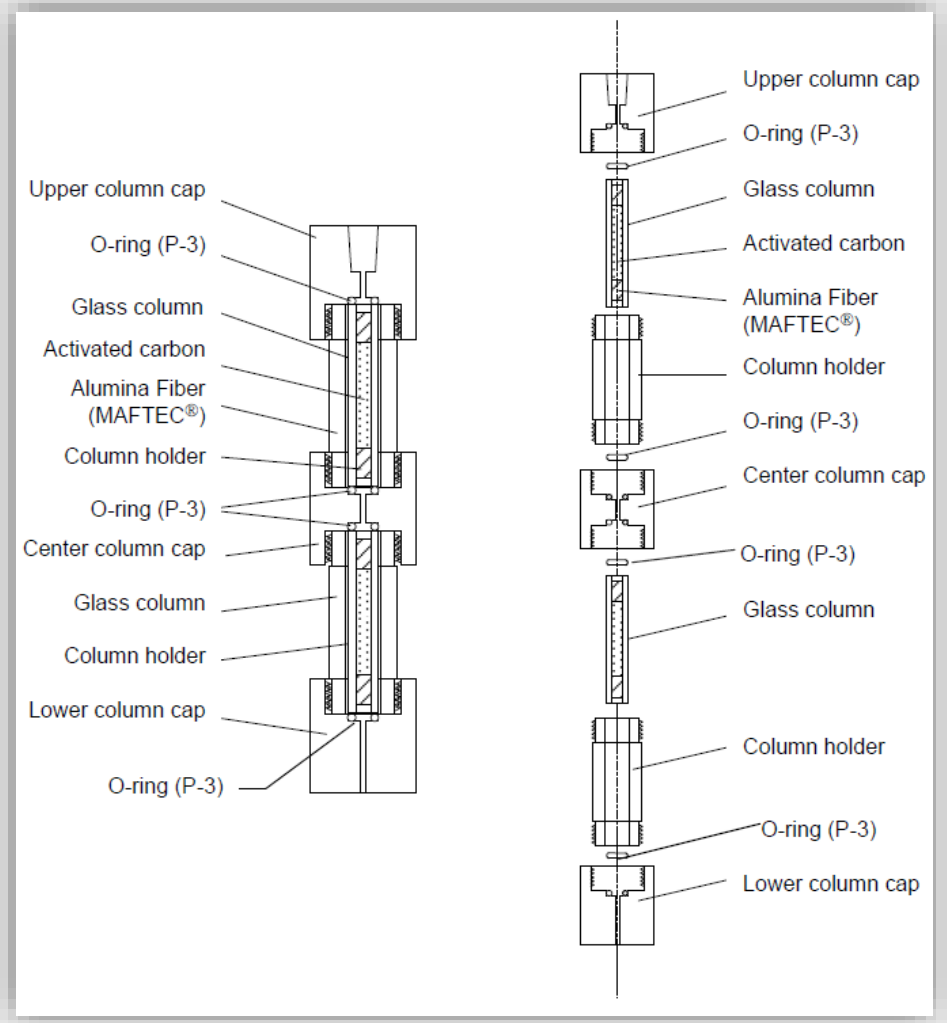


- Extracting up to 100mL sample provides improved detection (100X sample preconcentration)
- Complementary to LC-MS/MS methods as screening tool

Adsorbable Organic Fluorine (AOF)

HOW DOES IT WORK?

Analytik-Jena Model APU-SIM sample prep unit



Adsorbable Organic Fluorine (AOF)

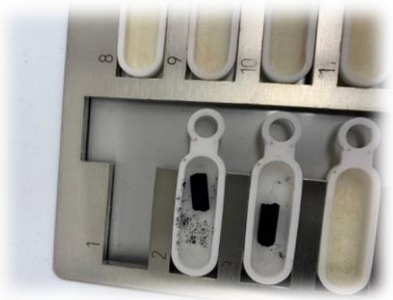
HOW DOES IT WORK?

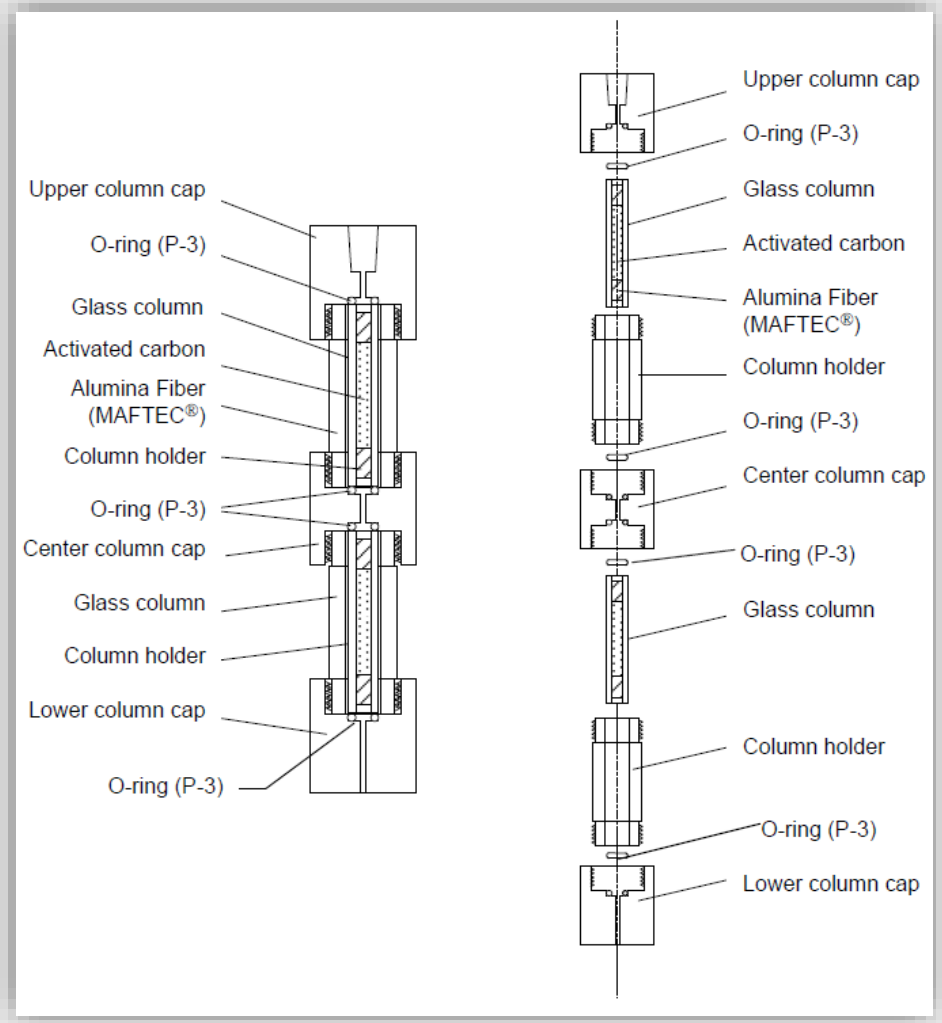
Pass 100mL of water sample through activated carbon (organic compounds will stick to carbon)

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

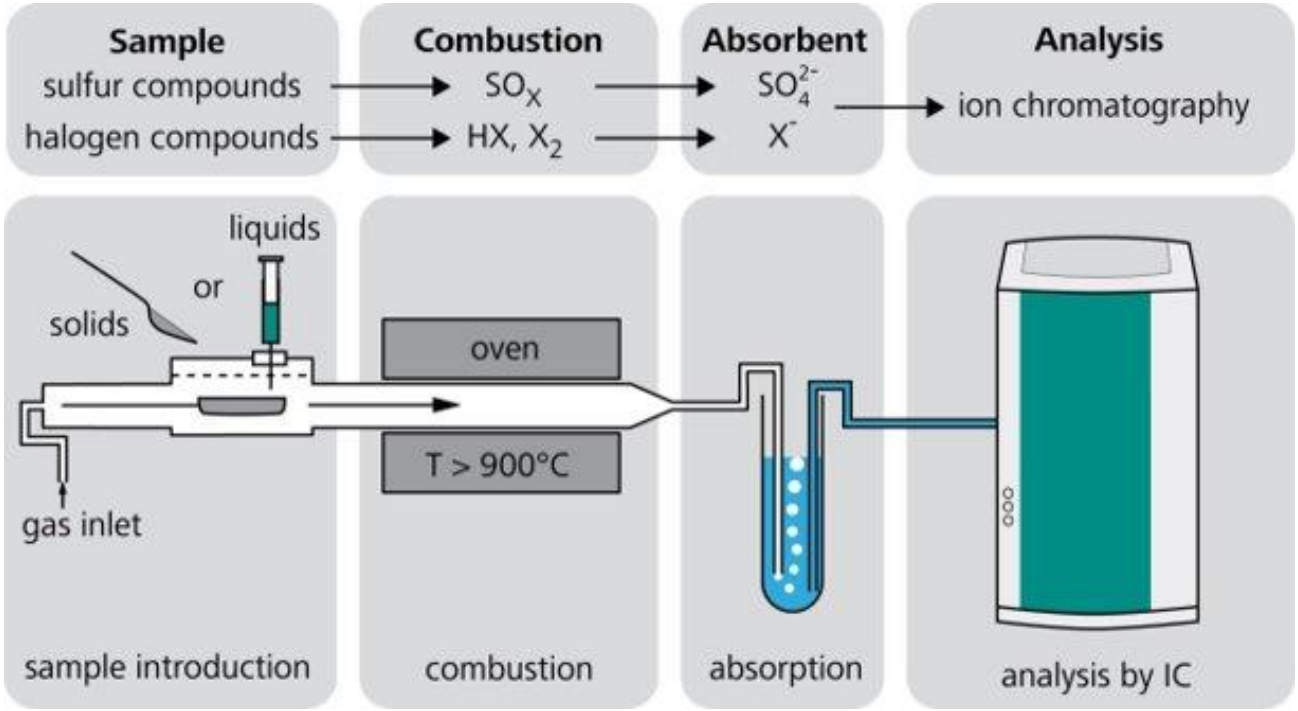
Nitrate Wash

Analyze carbon of each tube by Combustion IC



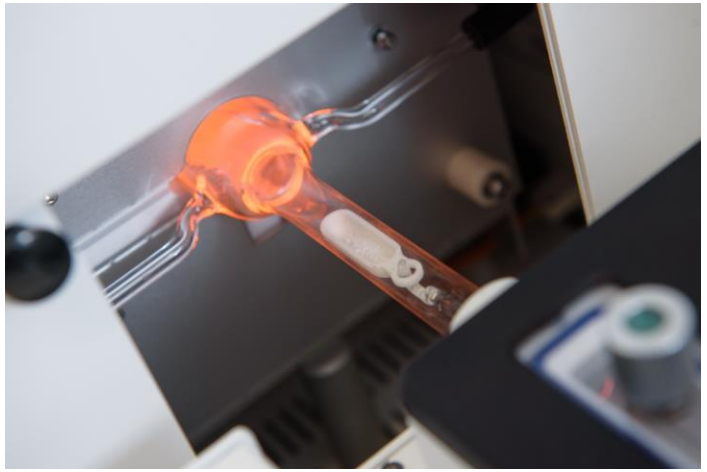


Combustion Ion Chromatography
HOW DOES IT WORK?



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:

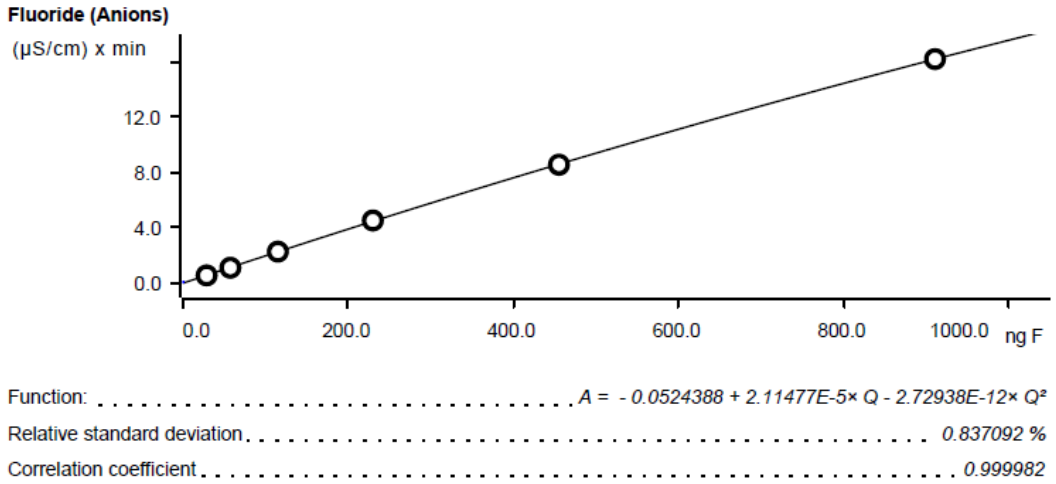
- Solids (Extracted charcoal)
- Liquids (standards, extracts, QC)

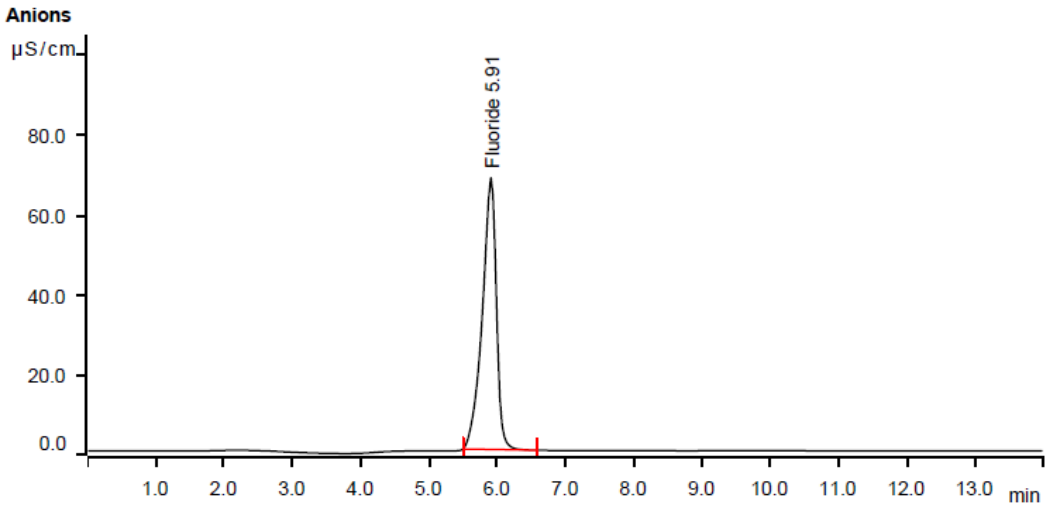
Flexible Calibration options

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





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

Calibration Options:

Calibration through Furnace (full CIC calibration)

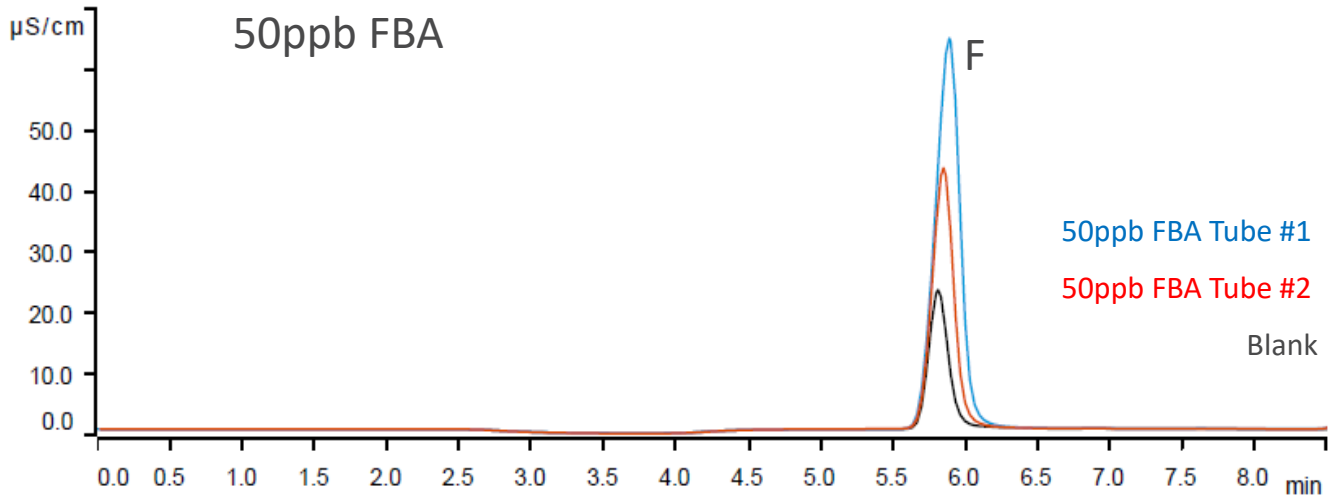
1) **Calibrate CIC** using a series of organic fluoride standards (*mass F* vs. *instrument response*)
2) **CIC Recovery Check:** Analyze an organic fluoride check standard through the entire combustion system to verify recovery of organic fluoride in CIC

   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

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



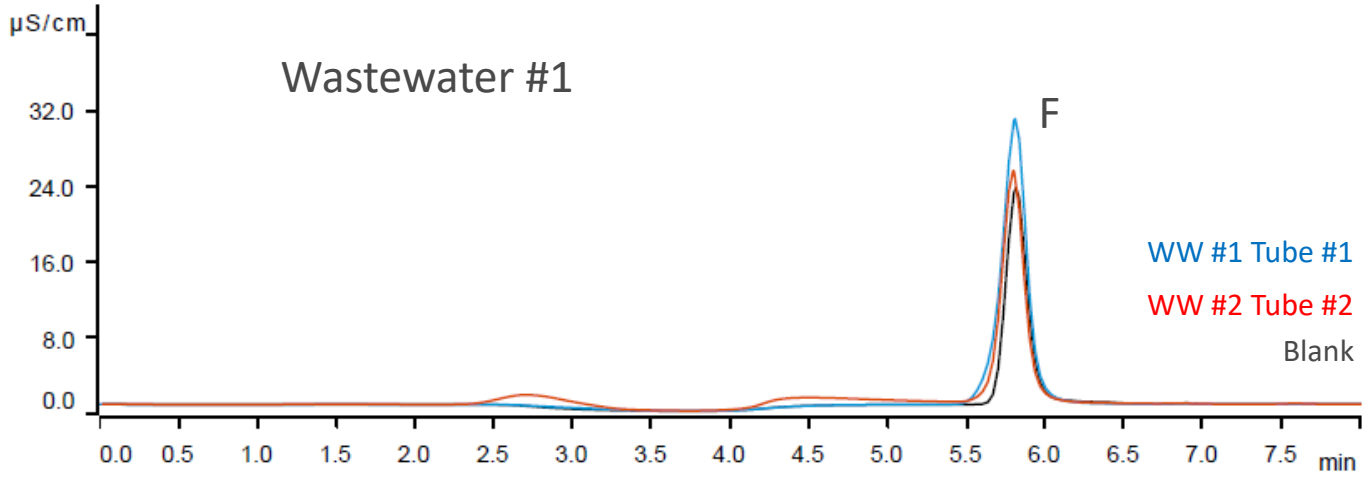
Sample ID	Total Mass F (ng) on-column	Concentration (µg/L, ppb)	% RSD	Recovery
Blank	15.7	1.1	5.9	-
5ppb FBA	221	**6.68***	8.9	134%
10ppb FBA	316	**11.16***	12.0	112%
50ppb FBA	1026	**49.85***	6.4	100%
100ppb FBA	1523	**84.65***	5.3	85%

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 Mass F (ng) on-column	Concentration (µg/L, ppb)	% RSD
Blank	15.7	1.1	5.9
Standard	237	**6.48***	0.9
Surface water	240	**6.68***	4.1
Wastewater 1	510	**15.65***	6.6
Wastewater 2	222	**6.17***	7.6

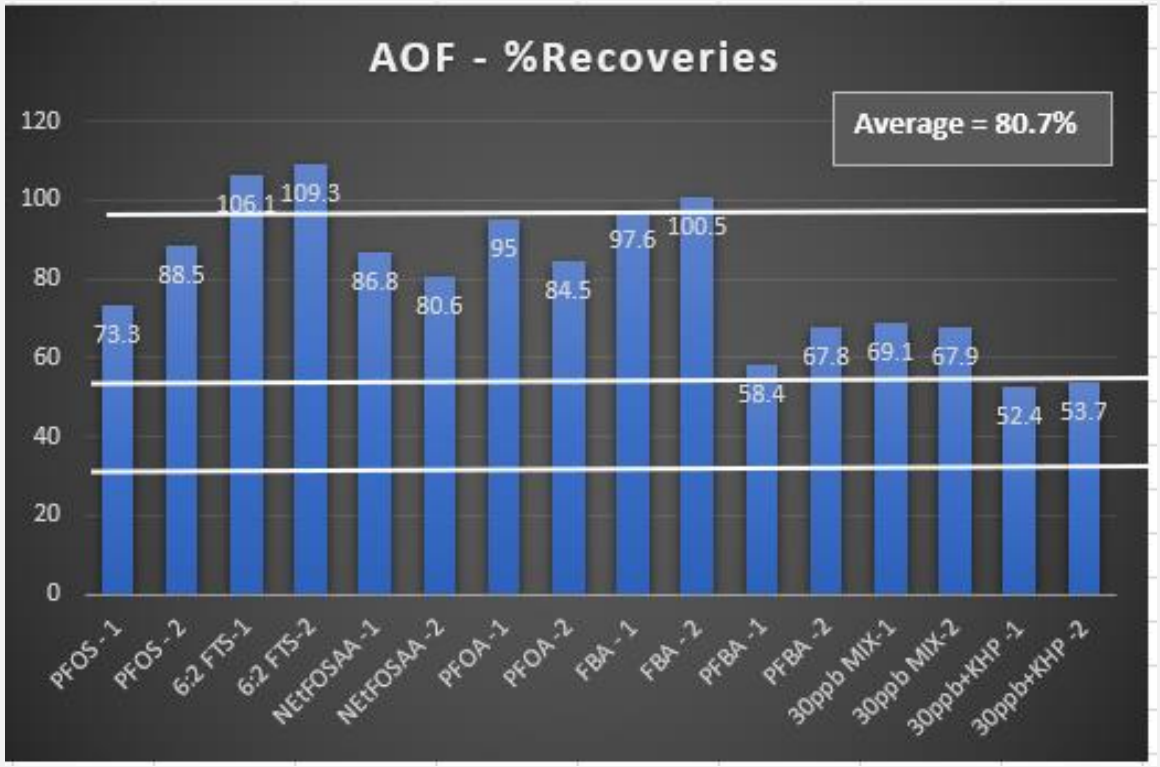
N = 4 samples
Total Peak Area, Total Mass F = sum of 2 tubes in series per sample
* Blank subtracted values

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%

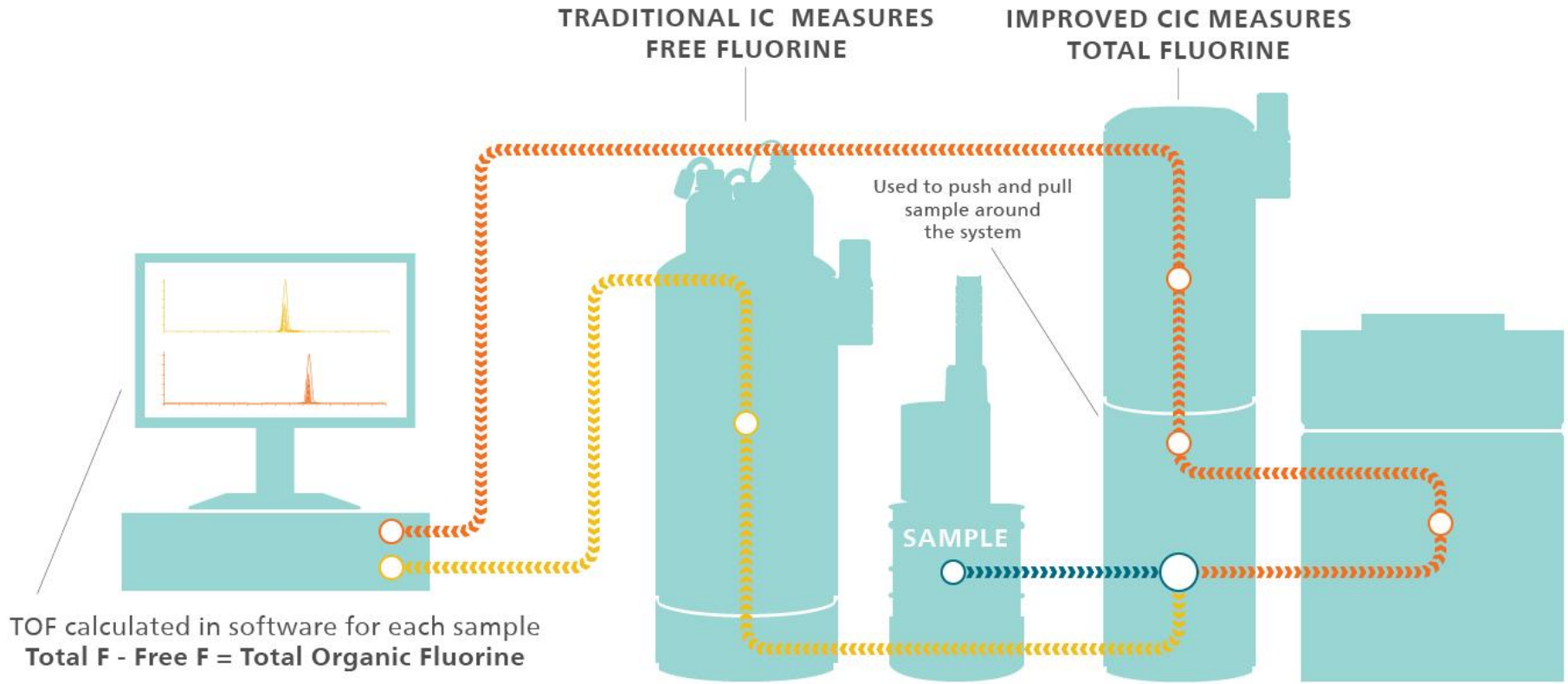
Profiler F
TOTAL FLUORINE ANALYZER

Metrohm

Direct Inject Aqueous sample configuration

How it Works

The system takes a single liquid sample and completes both a free fluoride analysis using direct IC and a total fluorine analysis incorporating proprietary combustion technology.



Total Fluorine = Total Organic Fluoride + Free Fluorine

Capture the Complete Profile

Total Fluorine

Free Fluoride

Total Organic Fluorine (TOF)

Configuration Parameters:

- Most tap water has 0.5 to 1 ppm free fluoride background from city treatment
- Background from free fluoride and other ions determines the TOF measurement range and limit of detection.
- Dilution (manual), inline sample preparation, and variable sample injection volume can be used to widen the measurement range, as necessary

Reporting & Data Analysis

FREE FLUORIDE

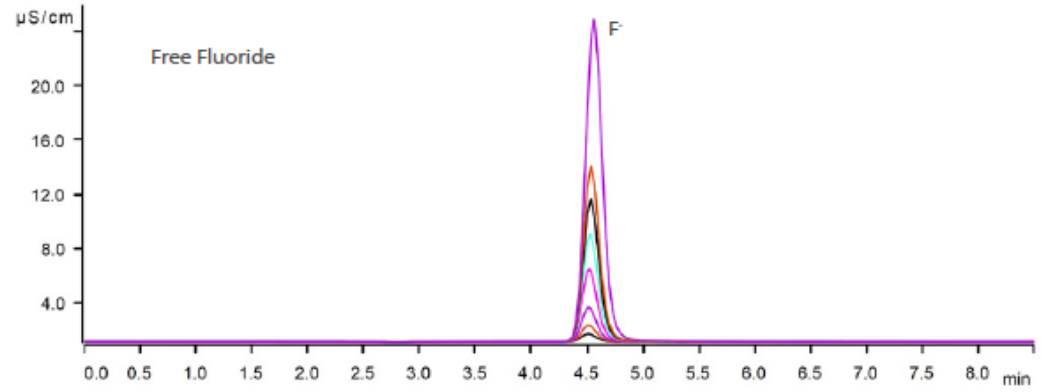
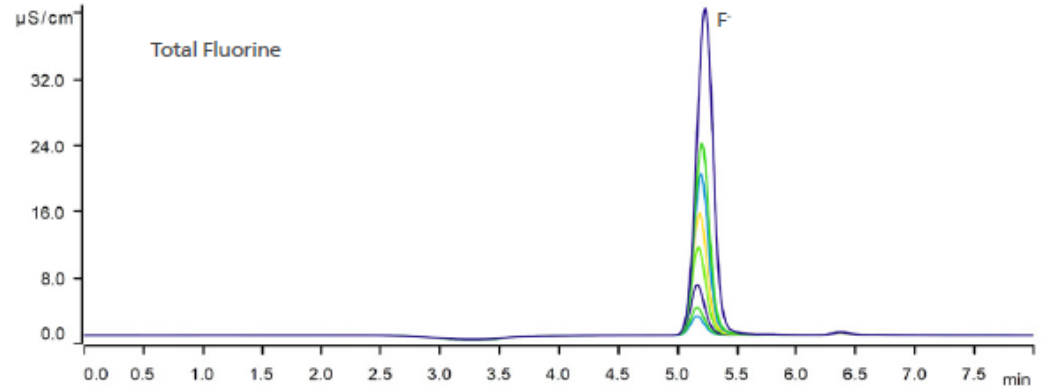


Figure 1.

TOTAL FLUORINE



- A single solution is used as a standard to calibrate both TF and FF
- Free Fluoride and Total Fluorine peak areas are determined automatically on one software platform - MagIC Net
- Single report is issued detailing free fluoride and total fluoride
- Methods and results are designed for entry level chemists

Real World Sample Data

Subset of Only 10 Samples

Sample description		Metrohm Profiler - F
(average of triplicate)	LCMSMS Results (by IDMS)	**Total Organic Fluoride**
	parts per billion (ppb)	
Real world Water Sample -1	0.0097	**150**
Real world Water Sample -2	0.0062	**130**
Real world Water Sample -3	0.8142	**570**
Real world Water Sample -4	2.586	**370**
Real world Water Sample -5	0	**217**
Real world Water Sample -6	2.8982	**65**
Real world Water Sample -7	0.0077	**40**
Real world Water Sample -8	0.2018	**120**
Real world Water Sample -9	0.2176	**156**
Real world Water Sample -10	0.0276	**147**

Every Single sample demonstrates higher Total Organic Fluoride ions compared to any other techniques in the market

Importance of Low Fluoride background

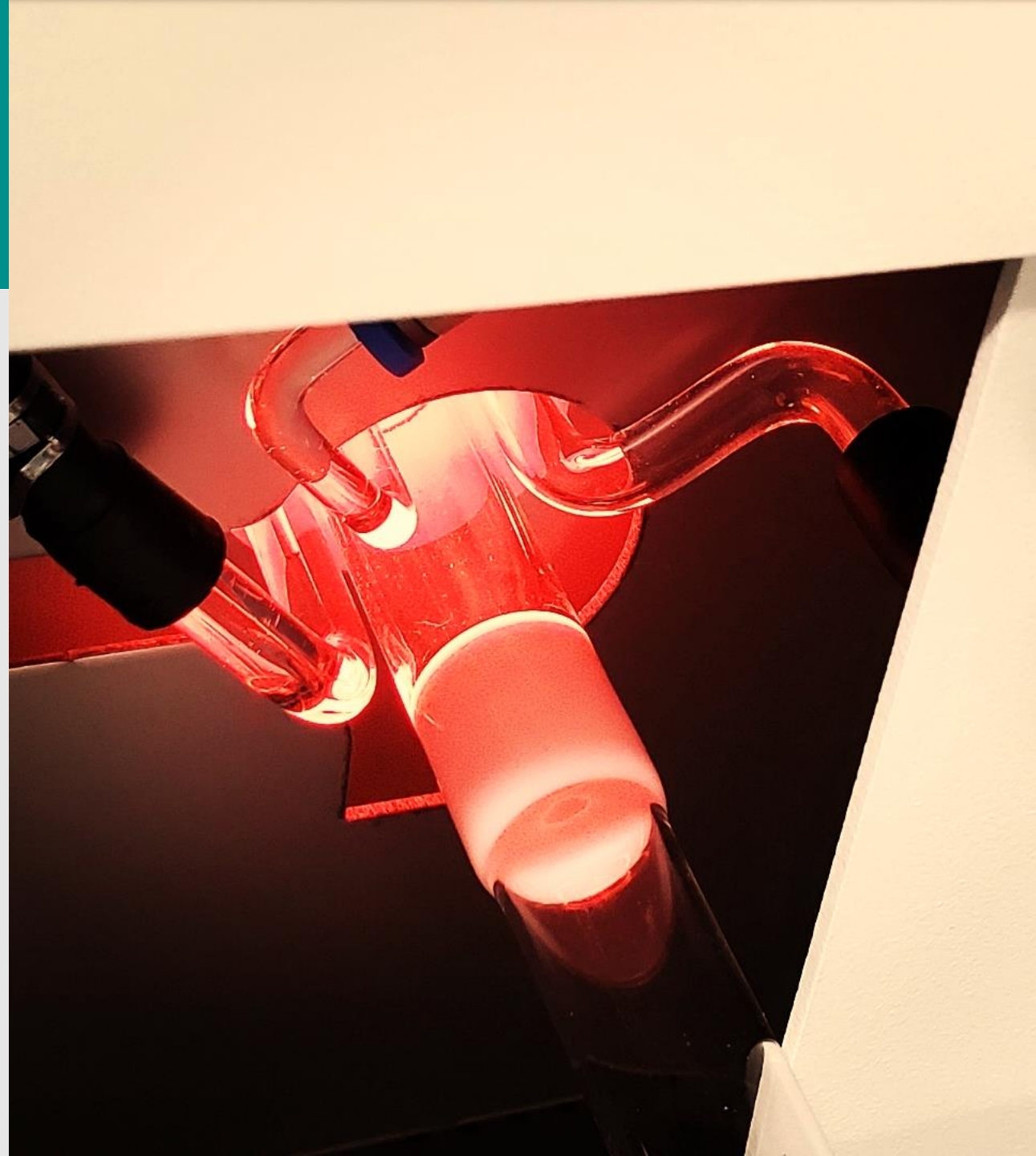
In the AOF – CIC technique, there are several places where background contribution can adversely affect results and sensitivity. *Minimizing the blank values are key.*

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

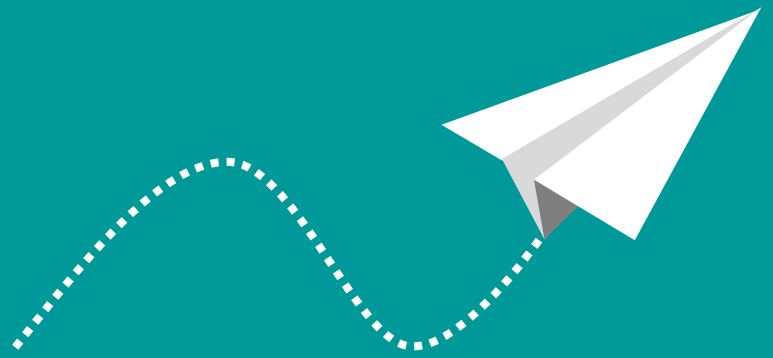


Metrohm CIC Advantage

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 jgandhi@metrohmusa.com