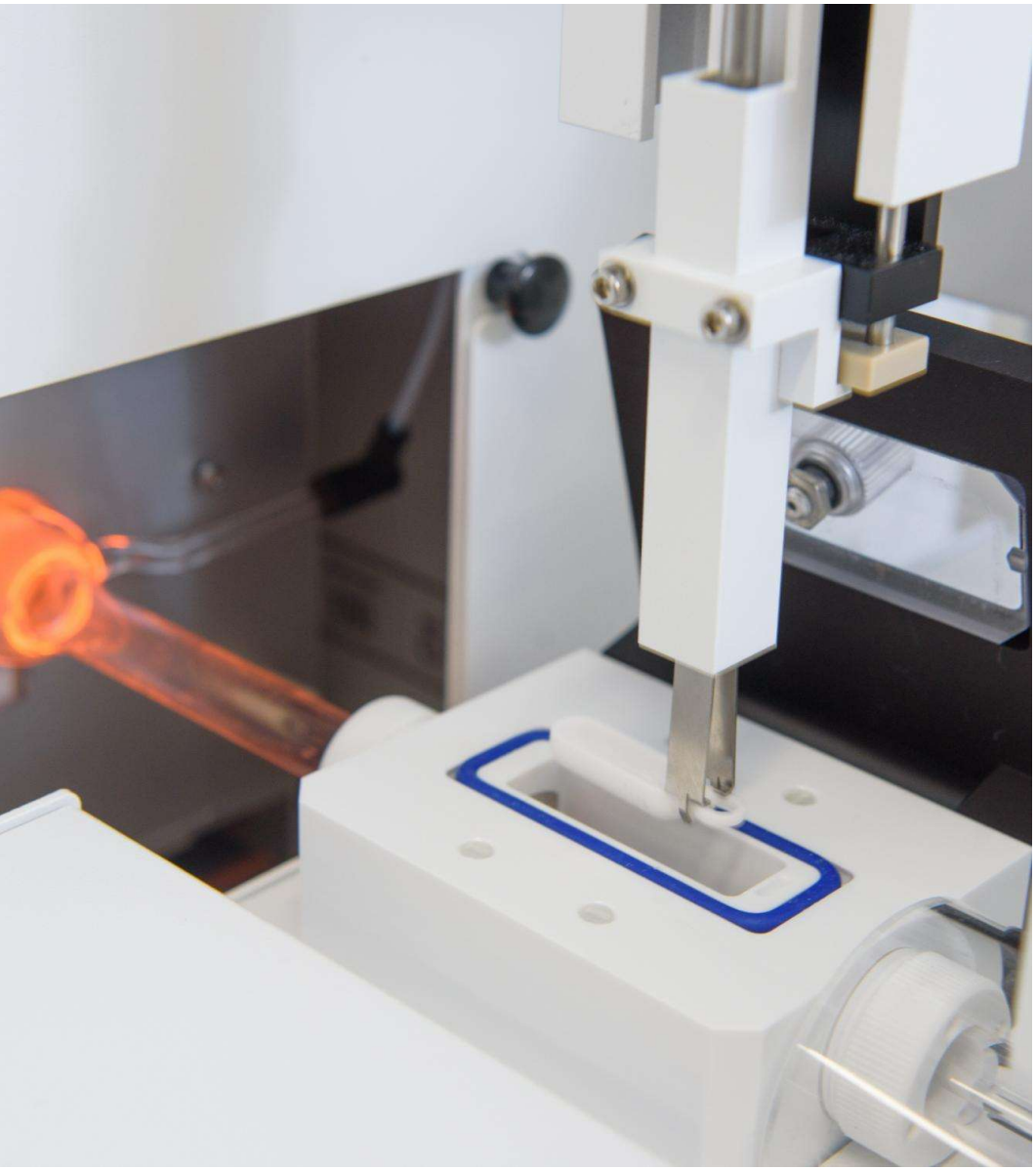


Novel Techniques in PFAS Monitoring

Comparing Non-Targeted Analysis Methods Utilizing Combustion Ion Chromatography

Adam Schanen
Metrohm USA
June 2024

Outline

- PFAS Overview
- Analysis techniques
- Targeted
- Non-Targeted
- Non-Targeted PFAS Analysis - Overview
- Combustion IC
- PFAS Analysis by Combustion IC
- Applications, Case Studies
- Comparison of Non-Targeted Methods
- Current & Future Research

Per- and polyfluoroalkyl substances (PFAS)

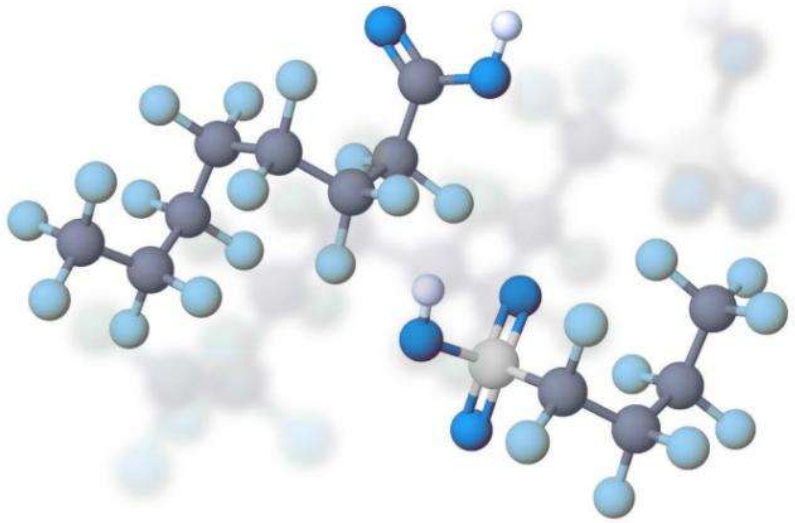
PFAS are manmade "forever" chemicals used in industry and consumer products.

"…human made chemical containing C-F bond…"

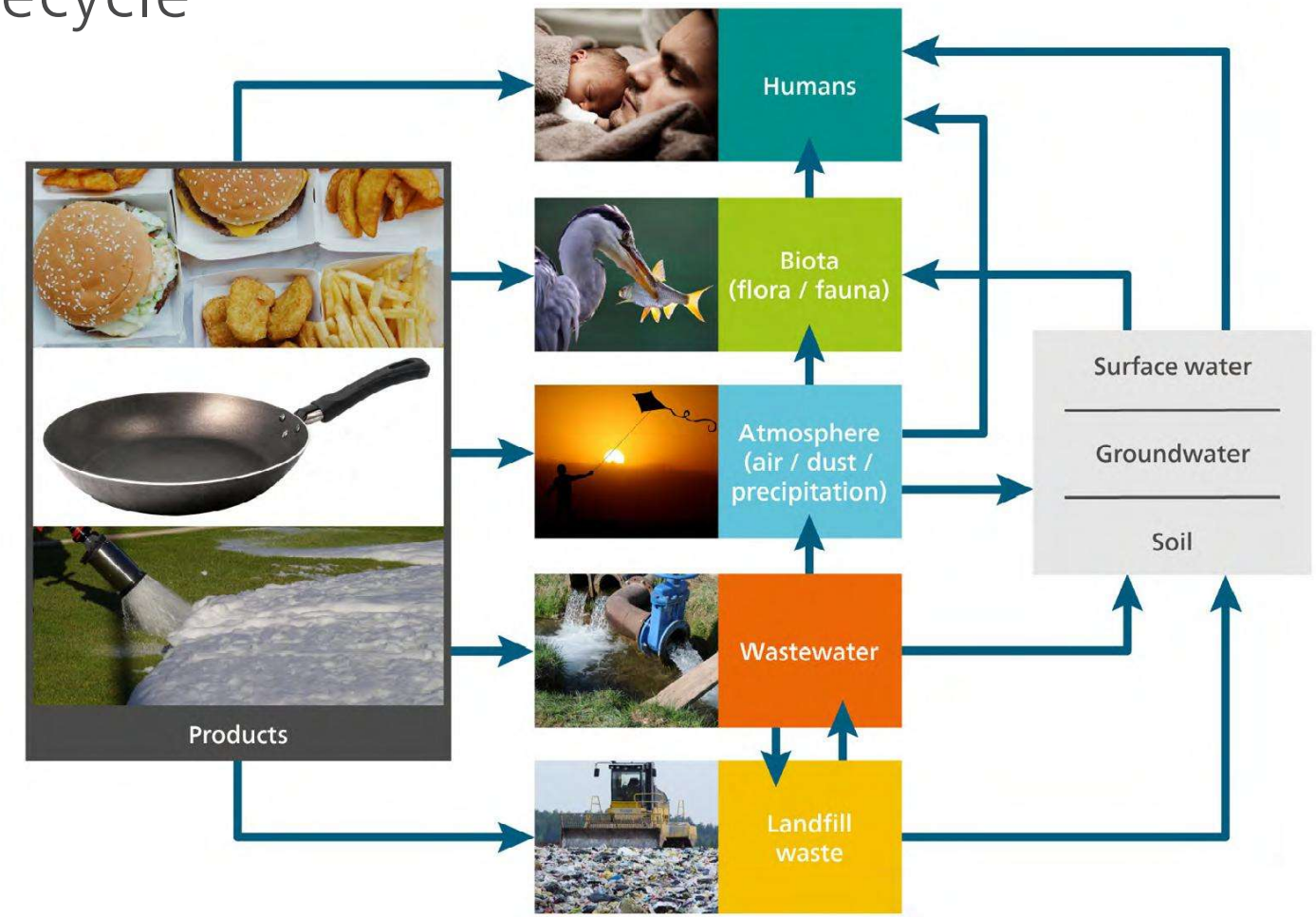
"…presence of a per- or polyfluorinated alkyl moiety…"

Exposure to PFAS have shown negative health effects.

Thousands of different PFAS-related compounds have been identified.



PFAS Lifecycle



Regulatory Landscape

Targeted methods for PFAS Analysis:

US EPA 533

- "… LC-MS/MS method for the determination of select per- and polyfluoroalkyl substances (PFAS) in drinking water"

US EPA 537.1

- "Determination of selected per- and polyfluorinated alkyl substances in drinking water…"

ASTM D7979

- "… determination of selected per- and polyfluoroalkyl substances (PFASS) in a water matrix…"

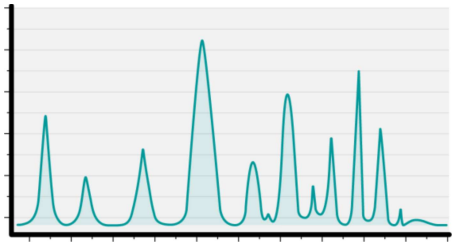
SW846 METHOD 8327

- "…method to determine selected per- and polyfluoroalkyl substances (PFAS) in prepared samples or sample extracts…"

Shortcomings of Targeted Techniques

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 fluorine content*, the indicator of overall impact

Approaches to Measuring PFAS

TARGETED ANALYSIS

- Measure selected PFAS compounds of particular concern using specific methods
- Measures PFAS (<100 compounds)
- Common technique: LC-MS/MS

NON-TARGETED ANALYSIS

- Assessment tool for total "impact" in environment
- Holistic approach - Measures total fluorine, organic fluorine

Non-Targeted PFAS Techniques

PARR BOMB

Offline combustion

Liquid extraction of combustate

Direct IC analysis

PIGE – PARTICLE INDUCED GAMMA RAY EMISSION

Spectroscopic technique

Highly specialized

19F NMR

Sum parameter of all fluorinated species by NMR

LC-HRMS

Time-of-flight Mass Spec

"Unknowns" characterization

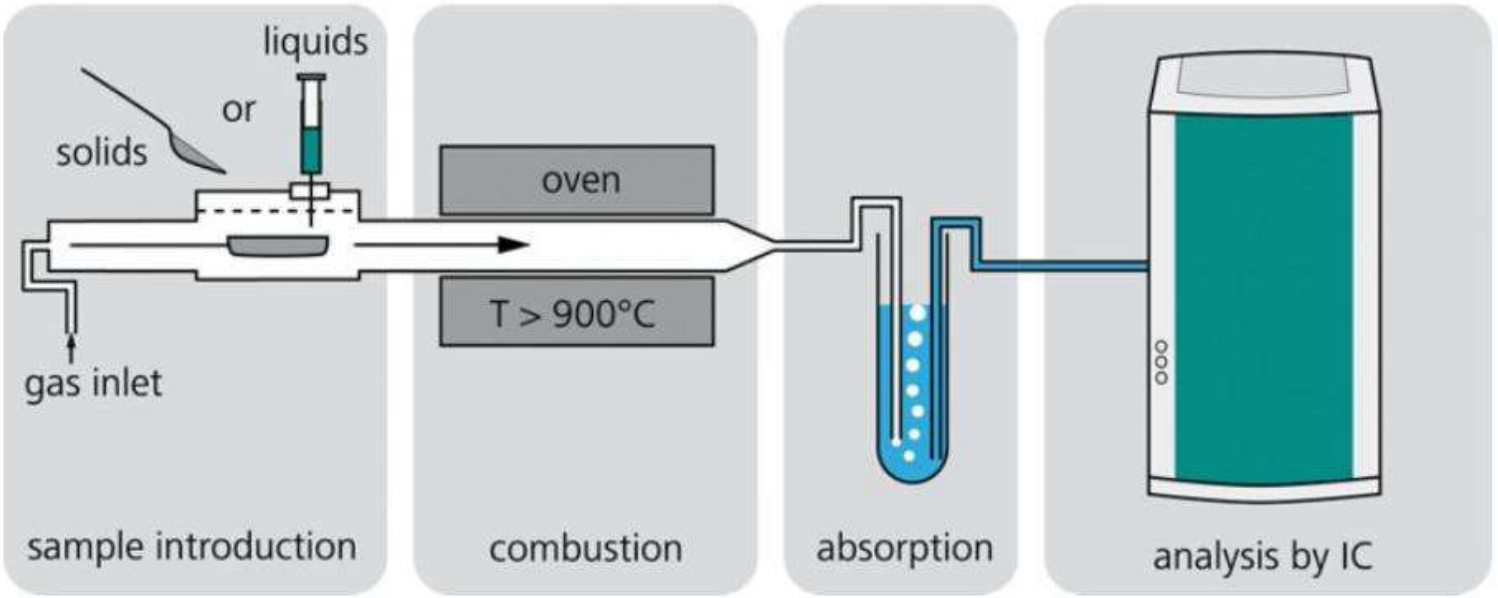
Compounds ID'ed one by one

Semiquantitative – no reference standard used

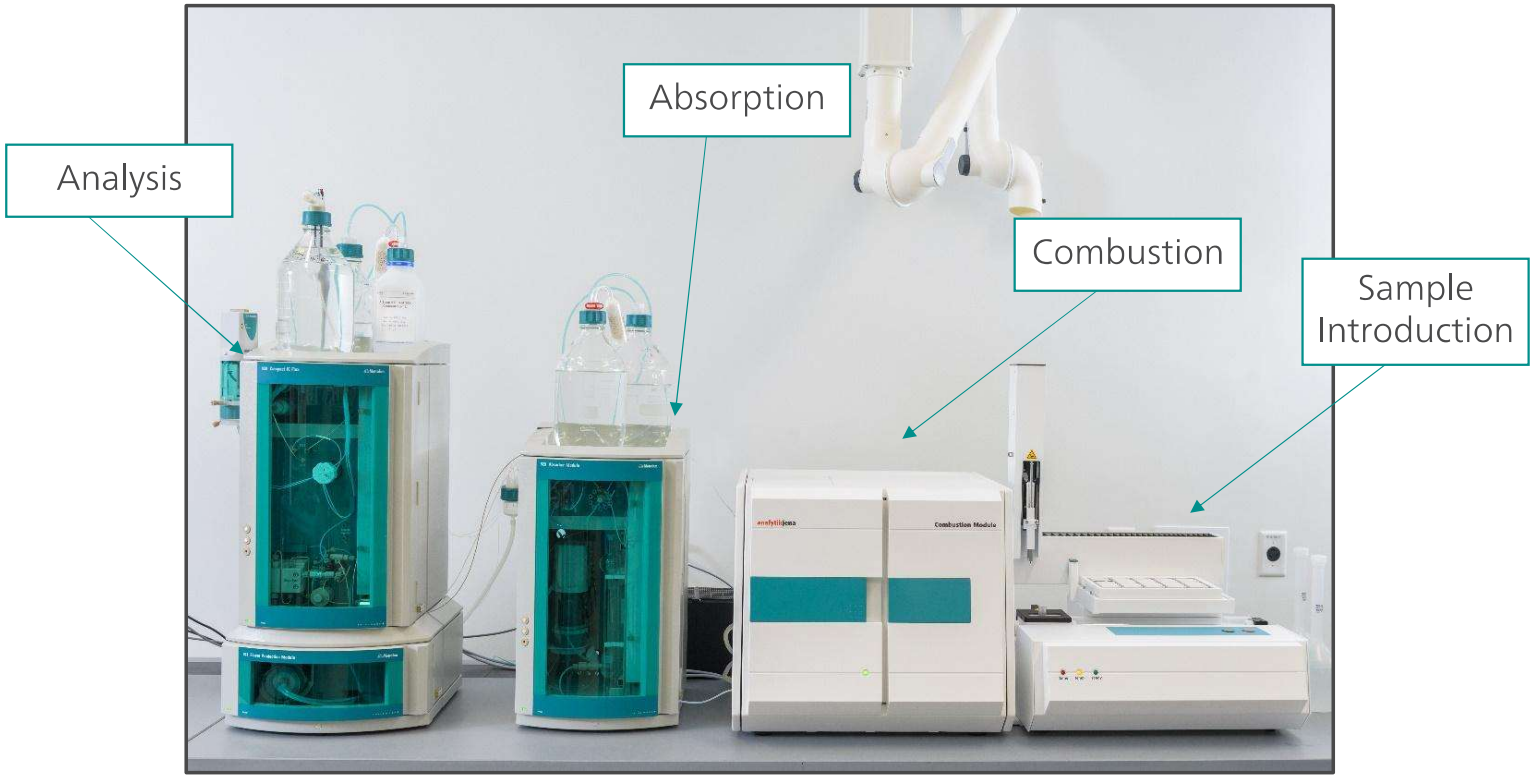
TOPS – TOTAL OXIDIZABLE PRECURSORS ASSAY

Offline chemical oxidation, sum of perfluorinated fragments as measured by LC-MS

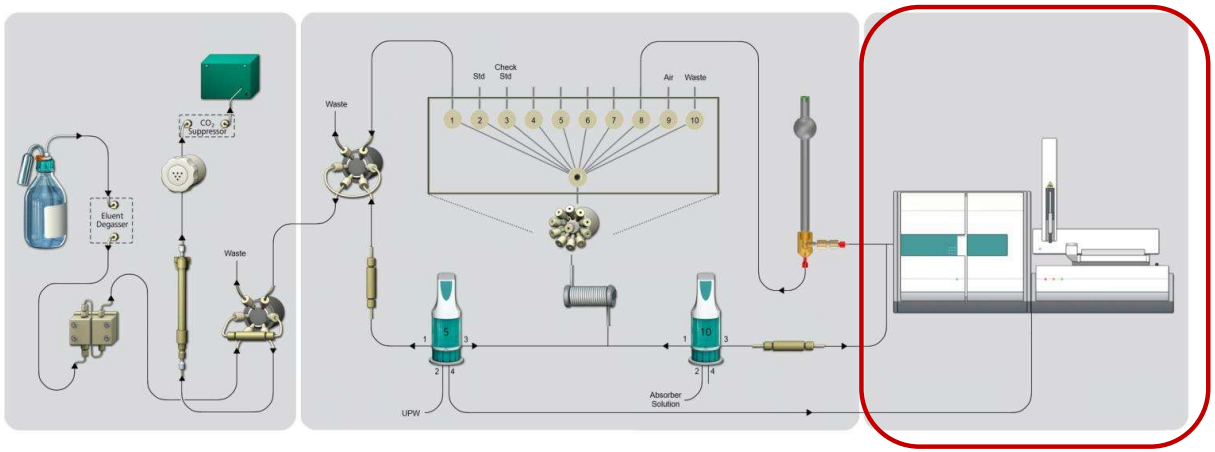
Combustion Ion Chromatography (CIC)



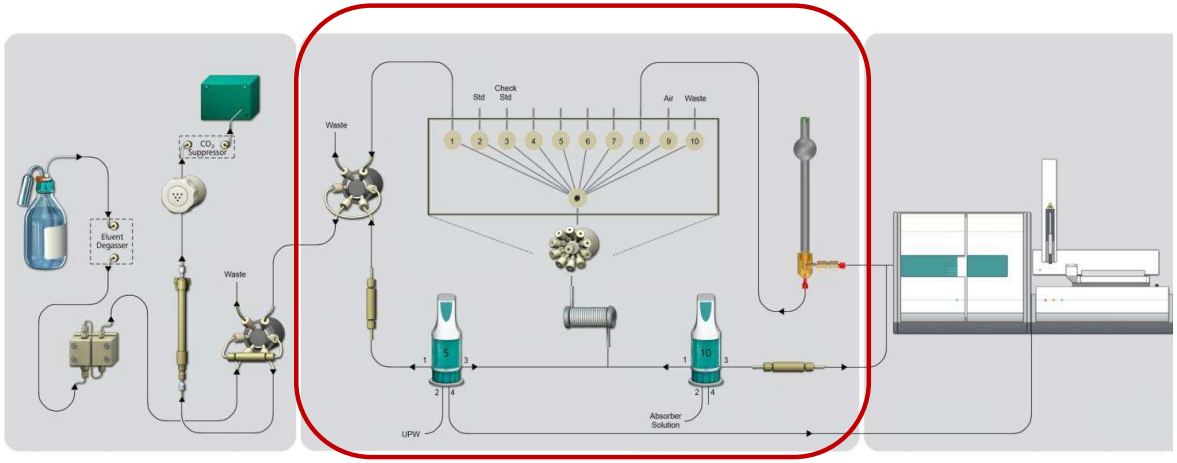
Combustion Ion Chromatography

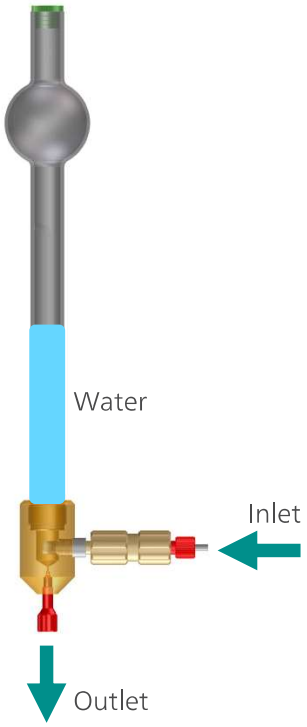


Combustion Ion Chromatography
Sample Introduction

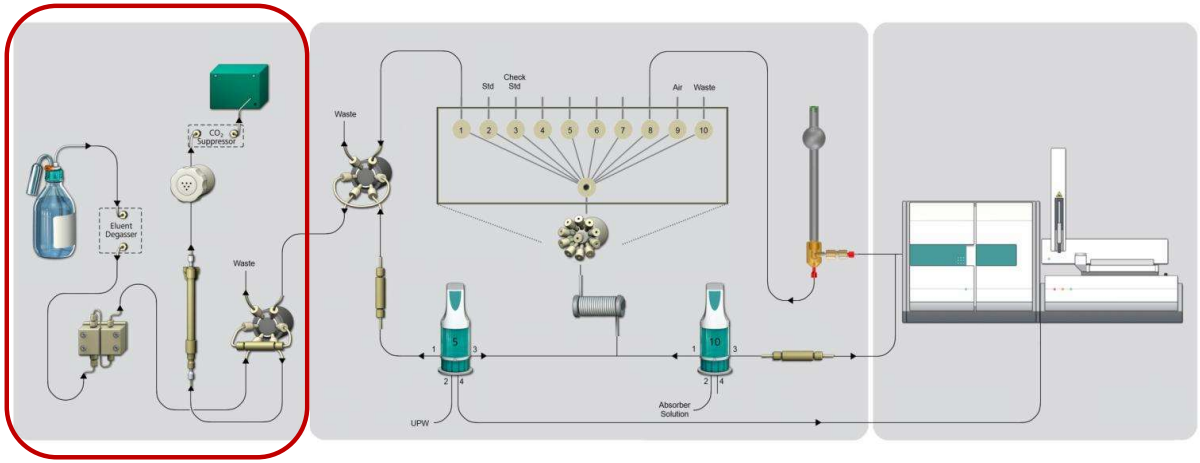


Combustion Ion Chromatography
Absorption





Combustion Ion Chromatography
IC Analysis



Non-Targeted PFAS Analysis by CIC

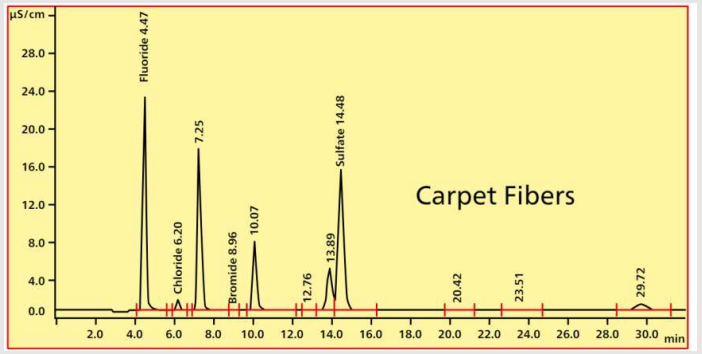
- Total Fluorine
- Adsorbable Organic Fluorine (AOF)
- Extractable Organic Fluorine (EOF)
- Total Organic Fluorine (TOF)

Total Fluorine (TF)

How does it work?

Sample weighed out, added directly to combustion boat (solids)
Sample added to HPLC vial, injected into dedicated combustion boat (liquids)

Analyze carbon of each tube by Combustion IC



Calibration Options

IC CALIBRATION (ONLY IC)

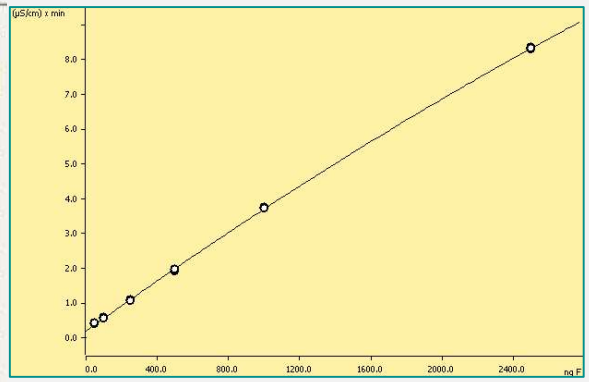
- **Calibrate IC** using a series of inorganic fluoride standards (*mass F vs. instrument response*)
- **IC Recovery Check:** Analyze IC check standard to verify recovery
- **CIC Recovery Check:** Analyze an organic fluoride check standard through the entire combustion system to verify recovery of organic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

FULL CIC CALIBRATION

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

Calibration Data
TF

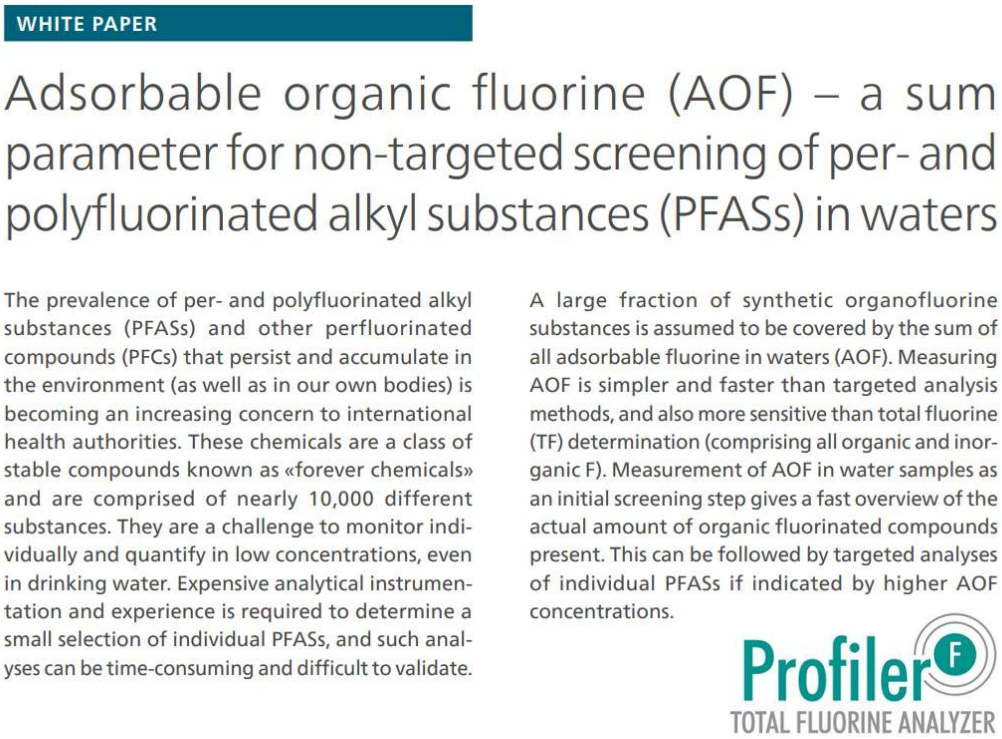
	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used	Conc.(calc.)	Conc.(dev.,%)
1	Standard 1	1	50.0	1000.0	1.0	1.0	0.406	0.5 ppm F	2020-08-25 22:00:39 UTC-5	☑	57.8	15.7
▶ 2	Standard 1	2	50.0	1000.0	1.0	1.0	0.423	0.5 ppm F	2020-08-25 23:40:26 UTC-5	☑	62.6	25.2
3	Standard 2	1	100.0	1000.0	1.0	1.0	0.572	1 ppm F as C4F9SO3K	2020-08-26 00:30:18 UTC-5	☑	103.2	3.2
4	Standard 2	2	100.0	1000.0	1.0	1.0	0.556	1 ppm F as C4F9SO3K	2020-08-26 01:20:10 UTC-5	☑	98.8	-1.2
5	Standard 2	3	100.0	1000.0	1.0	1.0	0.554	1 ppm F as C4F9SO3K	2020-08-26 02:10:08 UTC-5	☑	98.3	-1.7
6	Standard 3	1	250.0	1000.0	1.0	1.0	1.073	2.5 ppm F as C4F9SO3K	2020-08-26 03:00:06 UTC-5	☑	241.6	-3.3
7	Standard 3	2	250.0	1000.0	1.0	1.0	1.087	2.5 ppm F as C4F9SO3K	2020-08-26 03:50:03 UTC-5	☑	245.5	-1.8
8	Standard 3	3	250.0	1000.0	1.0	1.0	1.064	2.5 ppm F as C4F9SO3K	2020-08-26 04:39:59 UTC-5	☑	239.1	-4.3
9	Standard 4	1	500.0	1000.0	1.0	1.0	1.922	5 ppm F as C4F9SO3K	2020-08-26 05:29:53 UTC-5	☑	480.3	-3.9
10	Standard 4	2	500.0	1000.0	1.0	1.0	1.971	5 ppm F as C4F9SO3K	2020-08-26 06:19:47 UTC-5	☑	494.2	-1.2
11	Standard 4	3	500.0	1000.0	1.0	1.0	1.961	5 ppm F as C4F9SO3K	2020-08-26 07:09:39 UTC-5	☑	491.4	-1.7
12	Standard 5	1	1000.0	1000.0	1.0	1.0	3.729	10 ppm F as C4F9SO3K	2020-08-26 07:59:39 UTC-5	☑	1008.0	0.8
13	Standard 5	2	1000.0	1000.0	1.0	1.0	3.749	10 ppm F as C4F9SO3K	2020-08-26 08:49:40 UTC-5	☑	1014.2	1.4
14	Standard 5	3	1000.0	1000.0	1.0	1.0	3.731	10 ppm F as C4F9SO3K	2020-08-26 09:39:38 UTC-5	☑	1008.6	0.9
15	Standard 6	1	2500.0	1000.0	1.0	1.0	8.289	25 ppm F as C4F9SO3K	2020-08-26 10:29:37 UTC-5	☑	2489.5	-0.4
16	Standard 6	2	2500.0	1000.0	1.0	1.0	8.346	25 ppm F as C4F9SO3K	2020-08-26 11:19:35 UTC-5	☑	2509.6	0.4
17	Standard 6	3	2500.0	1000.0	1.0	1.0	8.311	25 ppm F as C4F9SO3K	2020-08-26 12:09:31 UTC-5	☑	2497.2	-0.1



Relative standard deviation	1.524%
Correlation coefficient	0.999945
Curve type	Quadratic
Weighting	1

50 – 2,500 ng F correlates to 0.5 – 25 ppm TF (100 mg sample size)

AOF with Combustion IC



WHITE PAPER

Adsorbable organic fluorine (AOF) – a sum parameter for non-targeted screening of per- and polyfluorinated alkyl substances (PFASs) in waters

The prevalence of per- and polyfluorinated alkyl substances (PFASs) and other perfluorinated compounds (PFCs) that persist and accumulate in the environment (as well as in our own bodies) is becoming an increasing concern to international health authorities. These chemicals are a class of stable compounds known as «forever chemicals» and are comprised of nearly 10,000 different substances. They are a challenge to monitor individually and quantify in low concentrations, even in drinking water. Expensive analytical instrumentation and experience is required to determine a small selection of individual PFASs, and such analyses can be time-consuming and difficult to validate.

A large fraction of synthetic organofluorine substances is assumed to be covered by the sum of all adsorbable fluorine in waters (AOF). Measuring AOF is simpler and faster than targeted analysis methods, and also more sensitive than total fluorine (TF) determination (comprising all organic and inorganic F). Measurement of AOF in water samples as an initial screening step gives a fast overview of the actual amount of organic fluorinated compounds present. This can be followed by targeted analyses of individual PFASs if indicated by higher AOF concentrations.

Profiler F
TOTAL FLUORINE ANALYZER

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

EPA METHOD 1621; 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
- Interlaboratory ruggedness study in progress

DIN 38409-59

Determination of adsorbable organically bound fluorine, chlorine, bromine and iodine (AOF, AOCl, AOBr, AOI) after combustion and ion chromatographic measurement

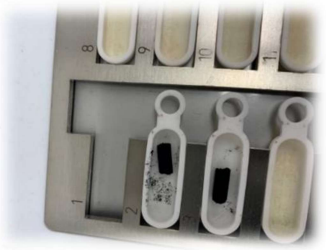
Adsorbable Organic Fluorine (AOF)
How does it work?

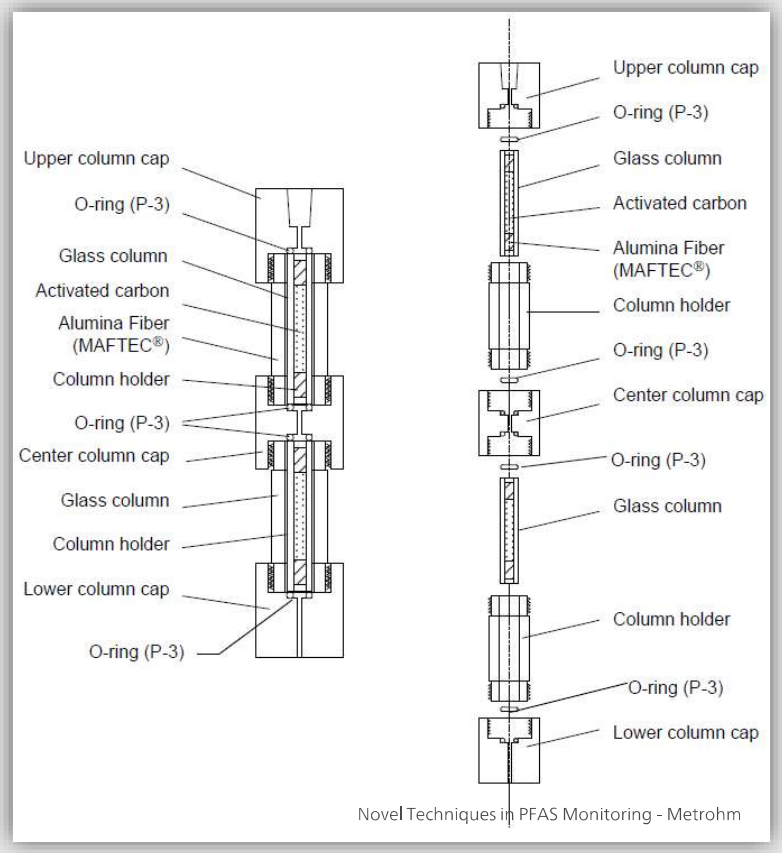
Pass 100mL of liquid sample through activated carbon (organic compounds will stick to carbon)

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

Nitrate Wash

Analyze carbon of each tube by Combustion IC

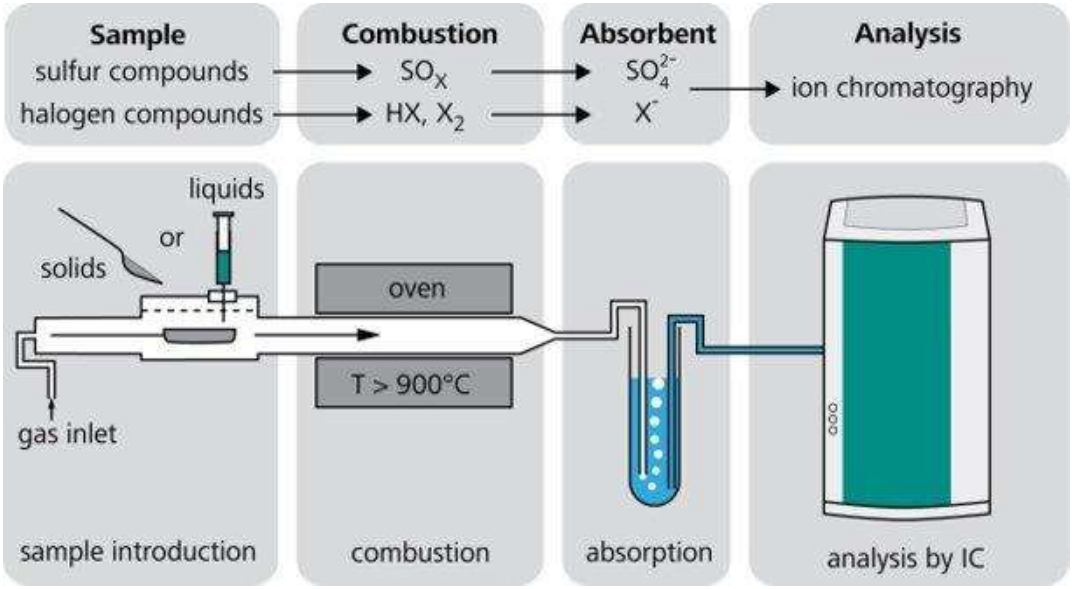




Automated Sample Prep Module for AOF Method

- Example SPE Manifold (6-position)
- Up to 100 mL volume of sample
- Sample is passed through charcoal tubes
- Tubes are automatically rinsed with sodium nitrate to remove free fluoride

Combustion IC for AOF
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^-

Calibration Data AOF

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used	Conc.(calc.)	Conc.(dev.,%)
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12	Standard 5	1	1000.0	1000.0	1.0	1.0	3.729	10 ppm F as C4F9SO3K	2020-08-26 07:59:39 UTC-5	☑	1008.0	0.8
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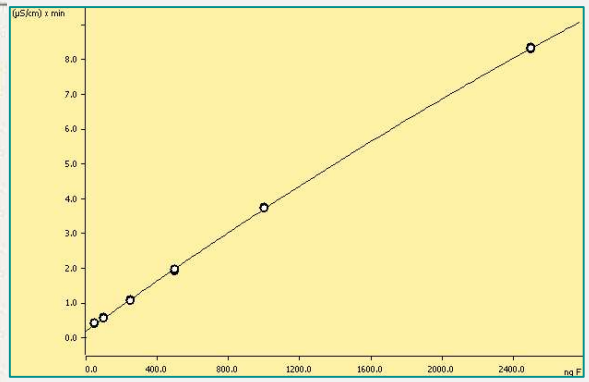


Relative standard deviation	1.524%
Correlation coefficient	0.999945
Curve type	Quadratic
Weighting	1

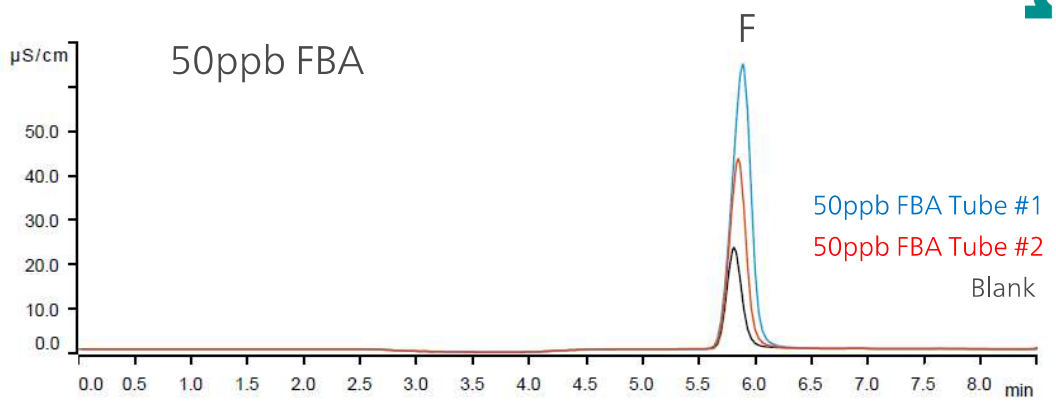
50 – 2,500 ng F correlates to 0.5 – 25 ppb AOF
(100 mL preconcentration, 50 mg carbon sample size)

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 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%

N = 2 samples

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

AOF – CIC Exemplary Data

Unknown Samples:

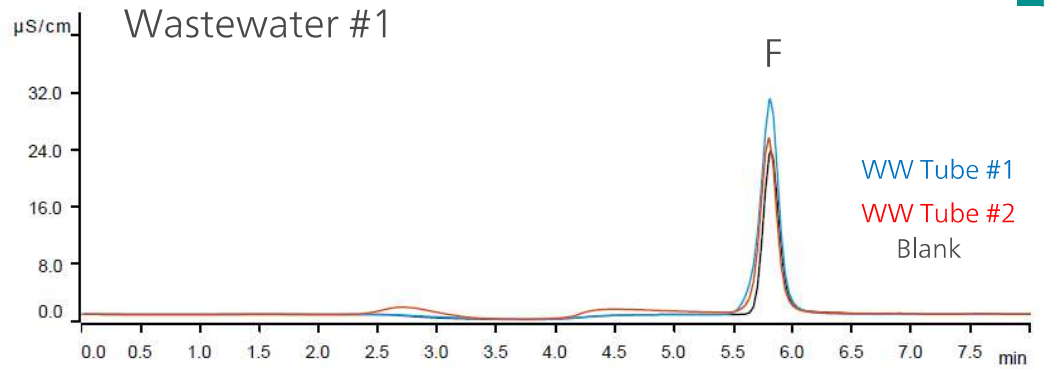
Study on Ruggedness, Reproducibility

Standard sample

Surface water sample

Wastewater Site #1

Wastewater Site #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
Site # 1	9.82	510	**15.65***	6.6
Site # 2	4.29	222	**6.17***	7.6

N = 4

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

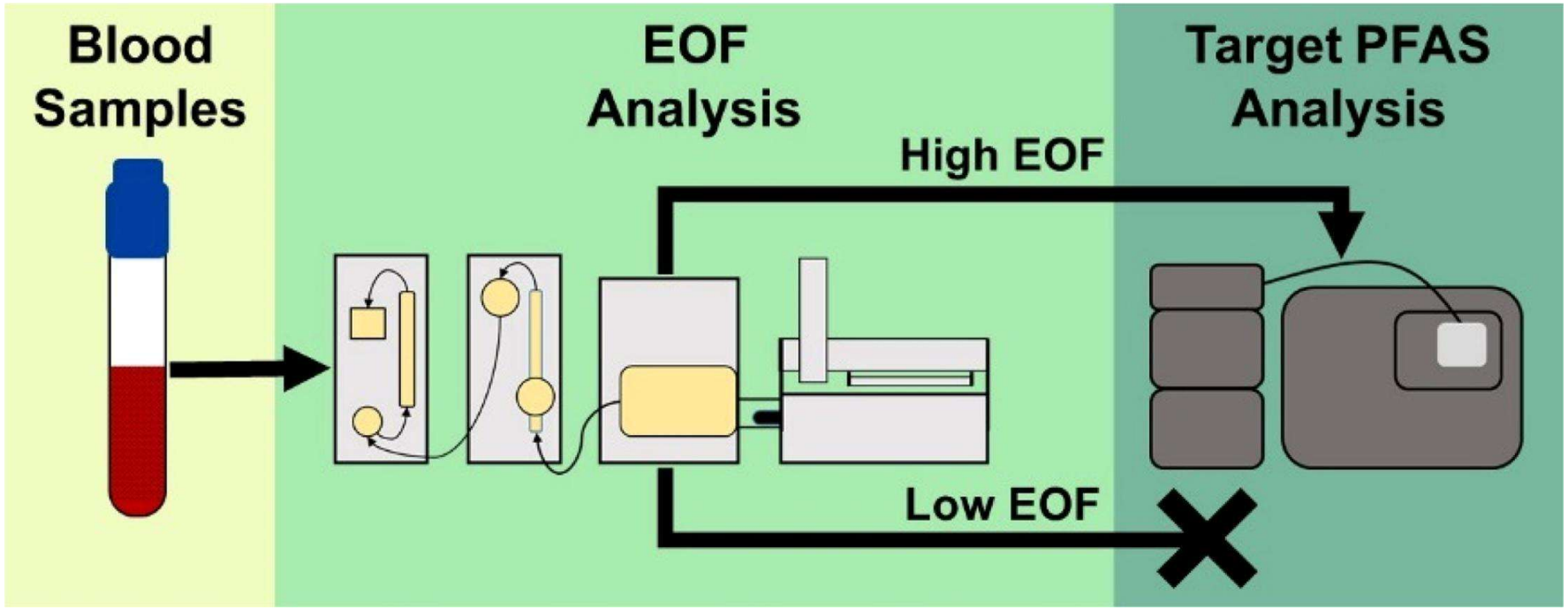
Extractable Organic Fluorine (EOF)

- Solid or liquid samples (100mg)
- Extracted e.g., with alkaline MeOH (pH=10)
- Filtered through SPE cartridge to remove inorganic fluoride
- Combustion of the eluate

ADVANTAGES

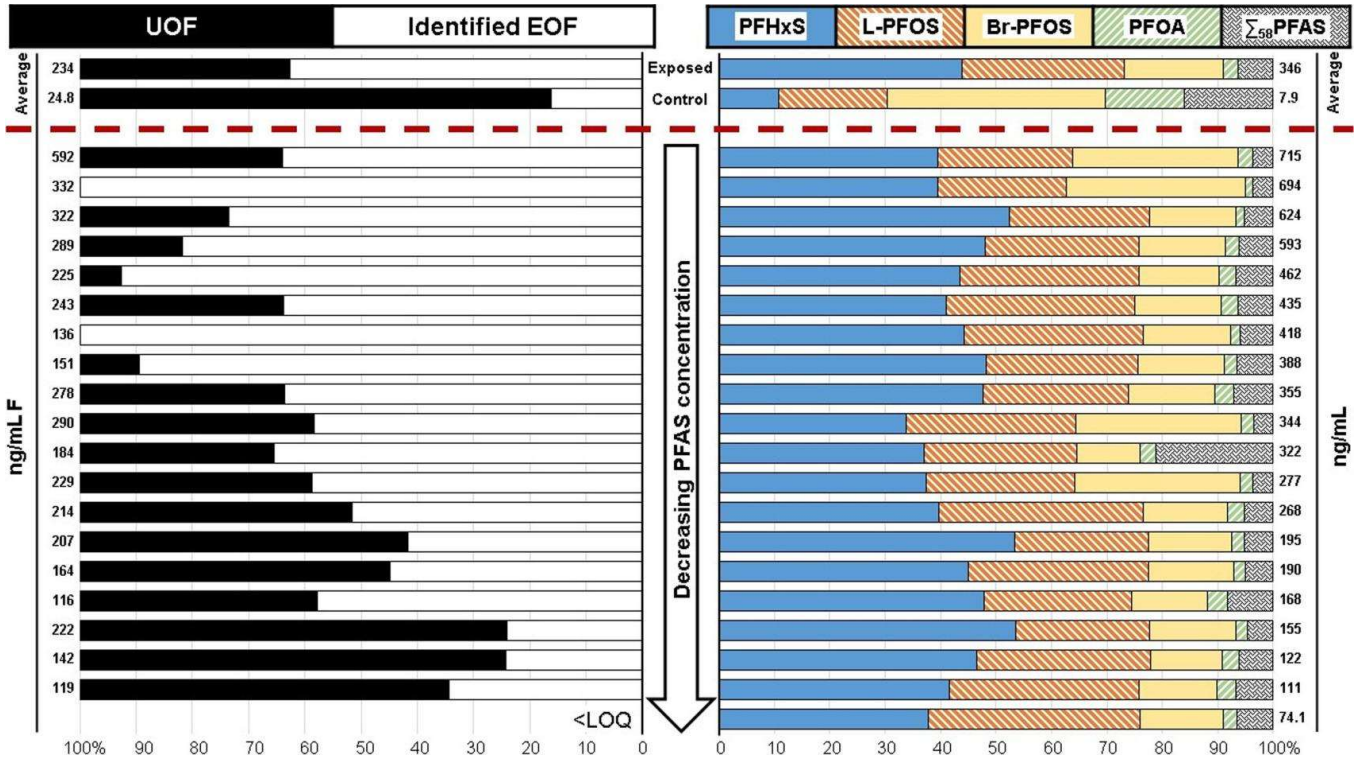
- Sensitive way to quantitate PFAS in difficult matrices
- Can be effective tool for targeting PFAS in solids (vs. TF by direct combustion) e.g. soil, landfill leachate, biosolids

Extractable Organic Fluorine (EOF)
Bioaccumulation



Aro et al. *Environment International.* 15 January 2022

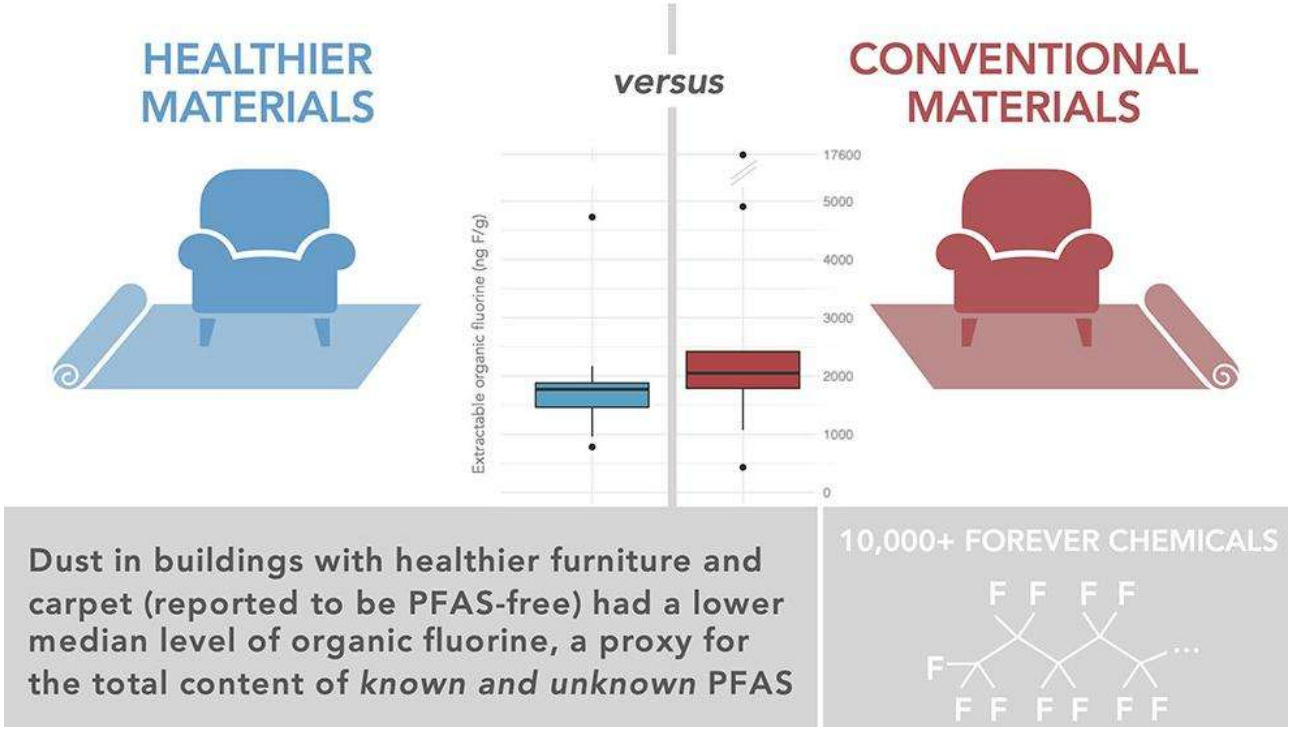
Extractable Organic Fluorine (EOF)
Bioaccumulation



Aro et al. *Environment International.* 15 January 2022

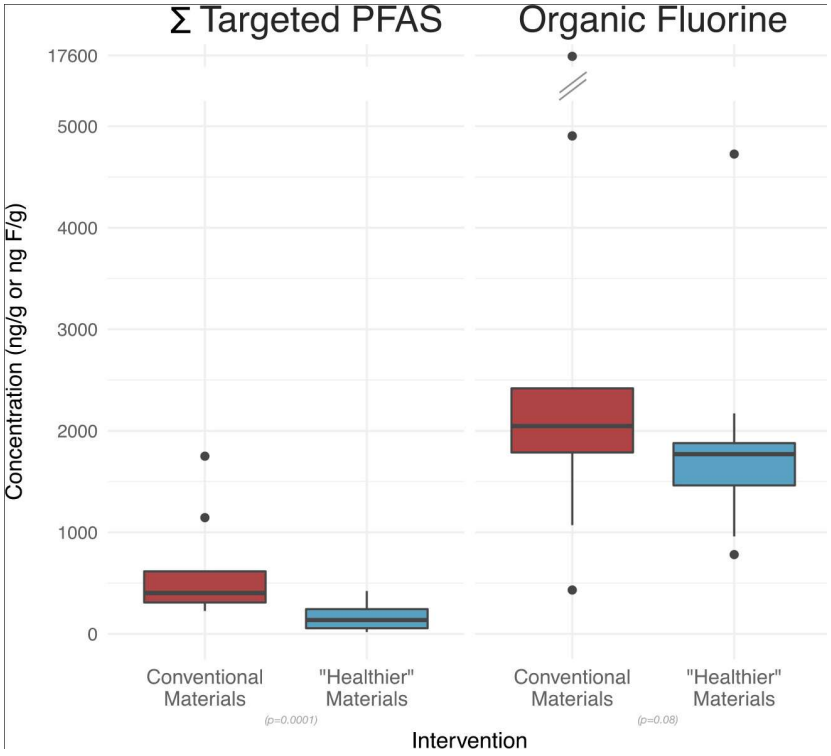
*Axes not normalized

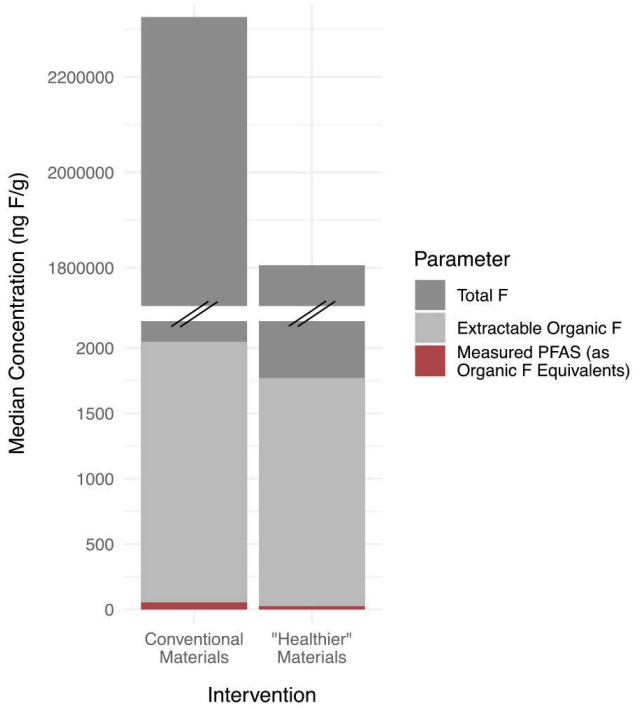
Extractable Organic Fluorine (EOF)
Consumer Products



Environ. Sci. Technol. 2022, 56, 23, 17090-17099

Extractable Organic Fluorine (EOF)
Consumer Products





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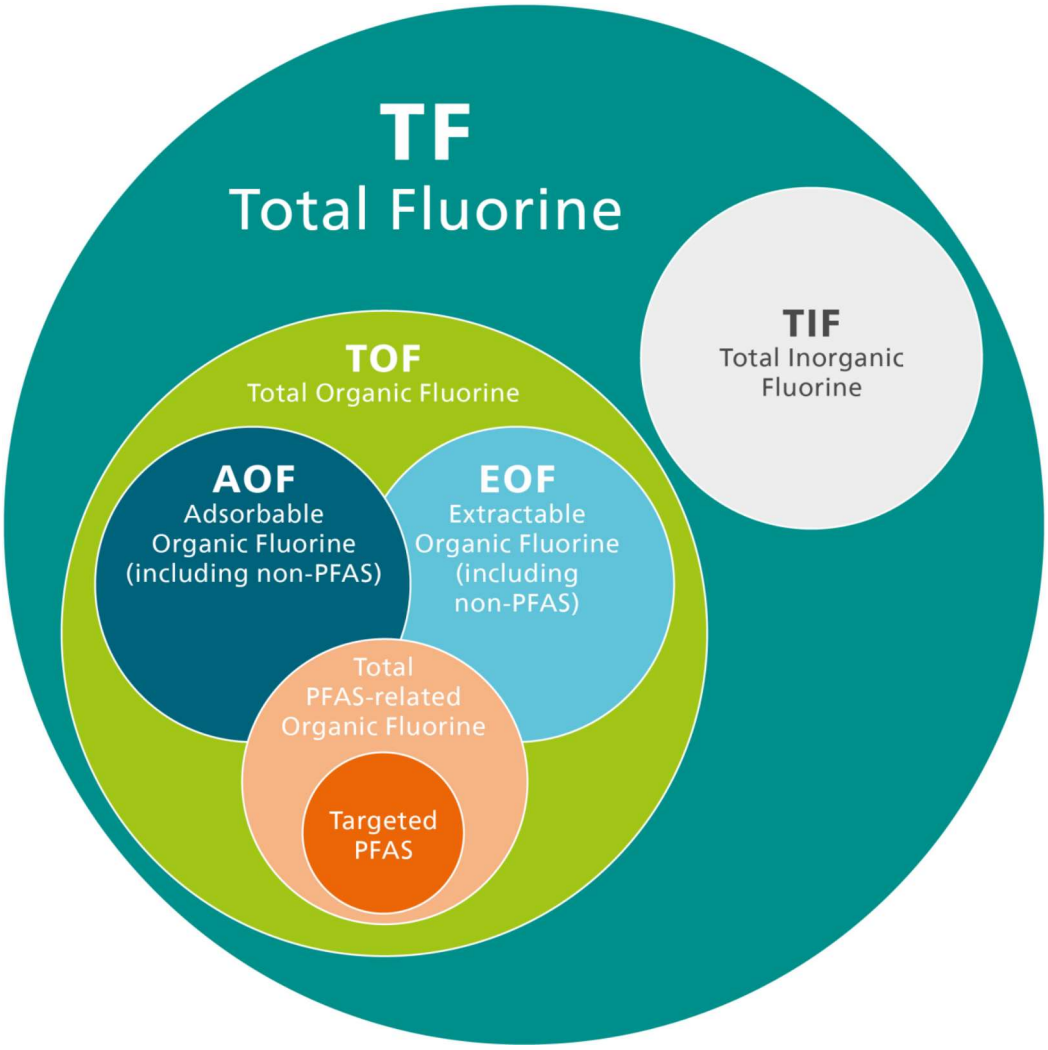
What About Total Organic Fluorine?



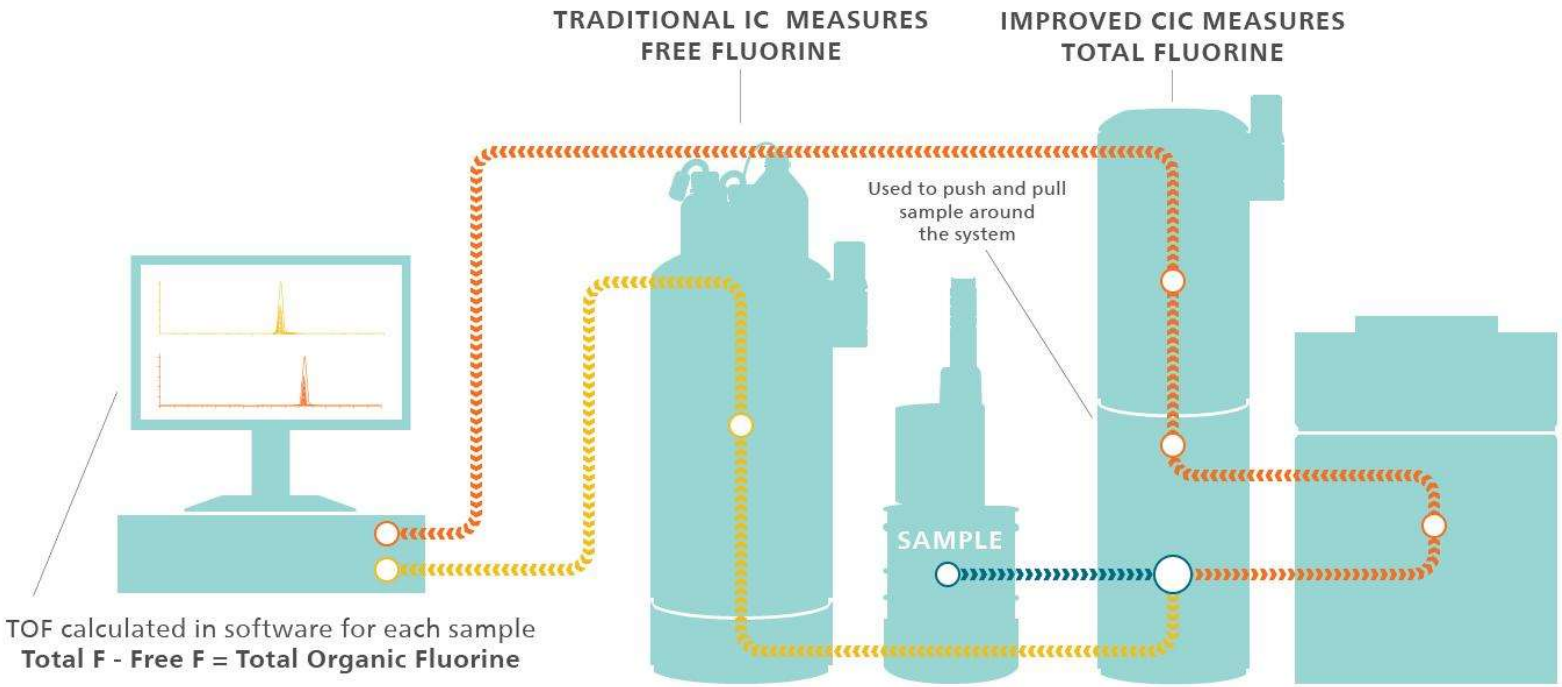
AOF, EOF ≠ TOF

AOF, EOF are dependent upon…

- AOF – Adsorptivity onto carbon media
- EOF – Extraction efficiency from sample/media
- TOF – Direct sample introduction, eliminate loss of PFAS in sample prep & analysis

Total Organic Fluorine (TOF) Analysis

- Free Fluorine (FF) by direct-inject IC
- Total Fluorine (TF) by Combustion IC
- Direct liquid introduction into CIC
- TOF = TF – IF



Total Organic Fluorine (TOF)

COMPOUND MEASUREMENT,
COMPOUND UNCERTAINTIES

LOQ = 20% of [Free Fluorine]

Drinking water (700 ppb FF) → 140 ppb LOQ

Intended use:

- Wastewater Influent/Effluent Monitoring
- Capture & Destruction processes

PFAS "MASS BALANCE"

Total Organic Fluorine
Reporting & Data Analysis

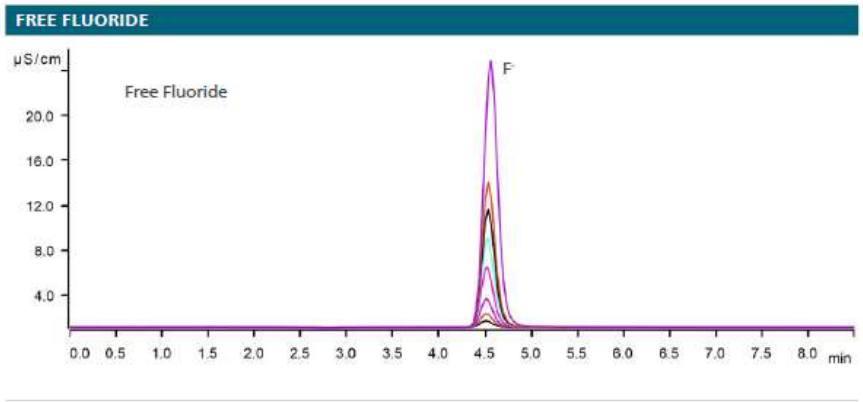
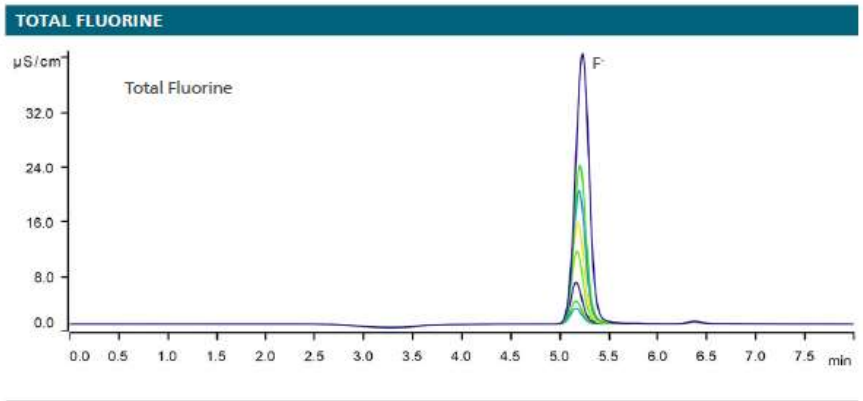


Figure 1.



- A single solution is used as a standard to calibrate both TF and FF
- Free Fluoride and Total Fluoride peak areas are determined in a single workplace
- Single report is issued detailing FF, TF, and TOF
- Methods and results are designed for entry level chemists

TOF in tap water

Metrohm

TOF = TF – TIF → 1.26 mg/L = 3.08 mg/L -1.82 mg/L

Free Fluoride interference, LOQ = 20% of [FF]

Drinking water, LOQ = 150 – 200 ng/mL

Can we remove FF?

Total Organic Fluorine
Exemplary Data

N=3 (all)	$\Sigma PFAS_{30}$ by LC-MS	Total Organic Fluoride
	Normalized, ppb as F	
Water Sample -1	0.0097	150
Water Sample -2	0.0062	130
Water Sample -3	0.8142	570
Water Sample -4	2.586	370
Water Sample -5	n.d.	217
Water Sample -6	2.8982	65
Water Sample -7	0.0077	40
Water Sample -8	0.2018	120
Water Sample -9	0.2176	156
Water Sample -10	0.0276	147

PFAS Analysis – A Comparison

	LC/MS-MS	TF	AOF	EOF	TOF
Strengths	Speciated Low-level analysis	No sample prep Matrix Versatility Sampling versatility Hardware versatility (TF, AOF, EOF)	Applicability/Importance Sensitivity Hardware versatility (TF, AOF, EOF)	Matrix Versatility Sensitivity Hardware versatility (TF, AOF, EOF)	Catch-all technique Fully automated No sample preparation Sample size (liquids) Wide calibration range
Limitations	Limited scope Complex data analysis	Non-specific for PFAS Lower sensitivity	Compound-dependent recovery Sample Prep Time Matrix-dependent	Compound-dependent recovery Sample Prep Time Matrix-dependent	Lower sensitivity Interferences

Managing CIC Performance

MINIMIZE BACKGROUND CONTRIBUTION

- Closed system
- Reagents, gases
- Vessels, consumables
- Laboratory environment

FIND BALANCE

- Sample size
- Interferences
- Combustion robustness

Current & Future Research

Combustion optimization

Tube packing material optimization

Increase sample sizes

Sample preparation

- Eliminate interferences – TOF
- Streamline preparation – AOF, EOF

Conclusion

- PFAS Overview
- Analysis techniques
- Targeted
- Non-Targeted
- Non-Targeted PFAS Analysis - Overview
- Combustion IC
- PFAS Analysis by Combustion IC
- Applications, Case Studies
- Comparison of Non-Targeted Methods
- Current & Future Research

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