



A Novel Approach to Total Organic Fluorine Analysis Using CIC

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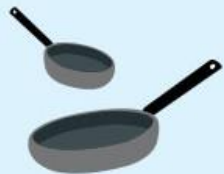
Today we will discuss

- **Background**
- **Approaches to measuring non-targeted PFAS**
- **Development of draft EPA Method 1621**
- **Limitations of Adsorbable Organic Fluorine (AOF) analysis**
- **Innovation for Total fluorine analysis with inorganic Fluoride removal**
- **Exemplary data for the innovative technique**
- **Next steps and 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.



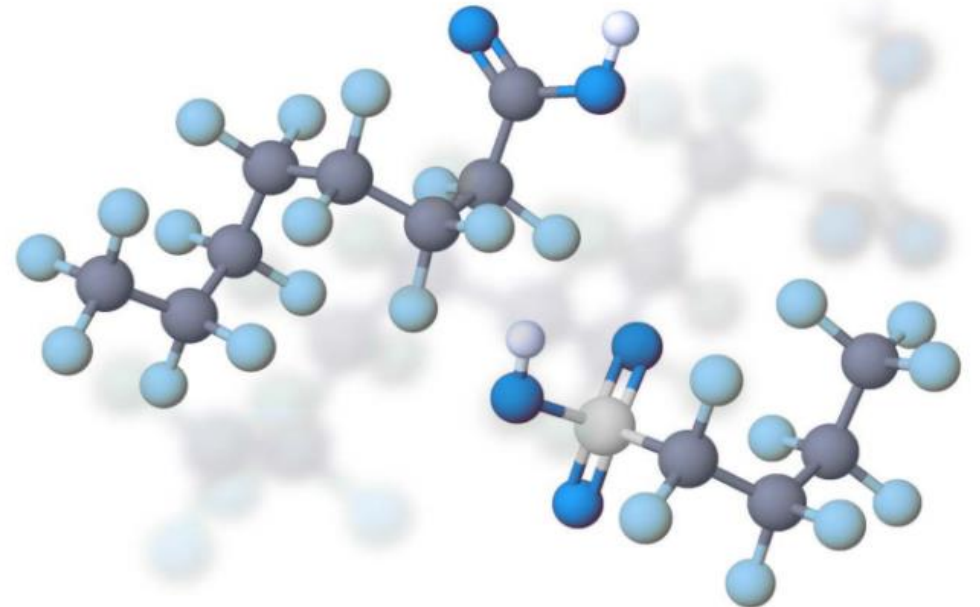
Nonstick
Cookware



Water-Repellant
Clothing



Firefighting
Foams



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
- US EPA Method 1621



Non-Targeted Analysis of Organic Fluorine with CIC

Direct Combustion

Direct combustion

- Combustion of sample in CIC to measure Total Fluorine in solids/liquids

Sample preparation

- None

Approximate detection limit

- 10 ppb or Less

Extractable Org F (EOF)

Capture & elute

- Combustion of extracted liquid sample in CIC to measure organic fluorine

concentrate

Approximate detection limit

- 2 - 5 ppb (standard CIC)
- 0.5 – 2 ppb (Profiler-F)

EPA Method 533/537
Draft EPA Method 1633

Adsorbable Org. F (AOF)

Capture & combust

- Combustion of charcoal w/ extracted liquid sample in CIC to measure organic

- Final wash with nitrate solution to remove inorganic fluoride

Approximate detection limit

- 2 - 5 ppb(standard CIC)
- 0.5 – 2 ppb (Profiler-F)

Draft EPA Method 1621
DIN 38409-59

Today, we will focus on this Innovative technique

What are limitations for AOF/EOF techniques?

AOF Technique:

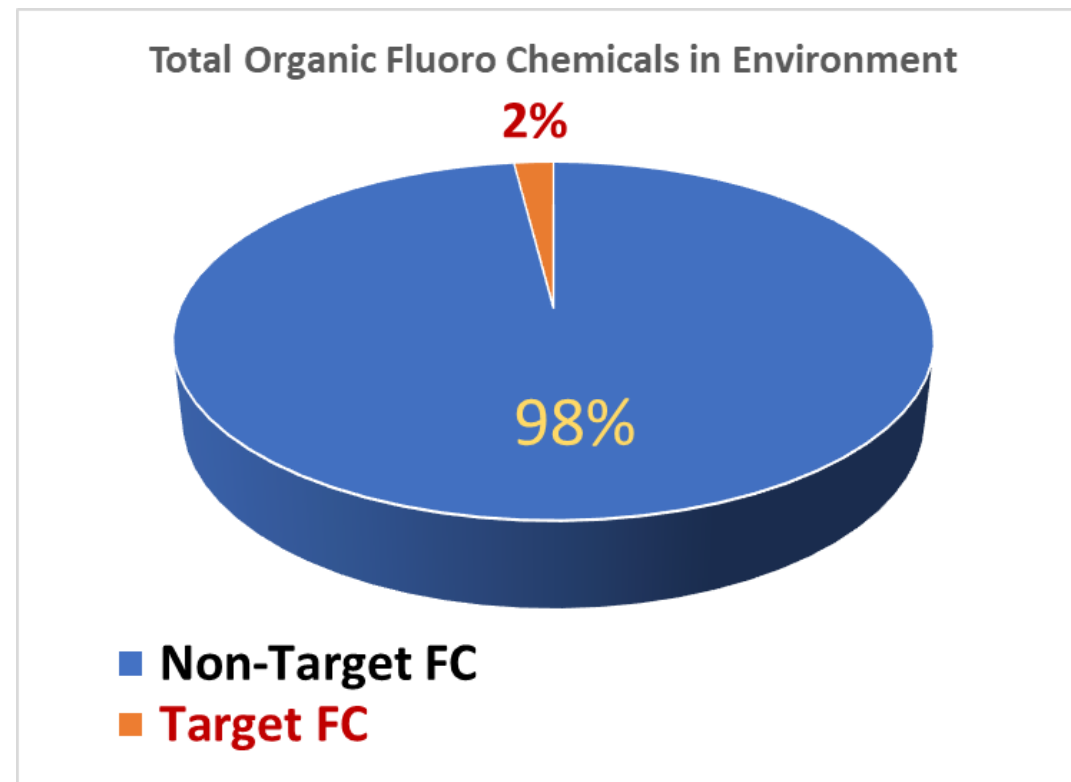
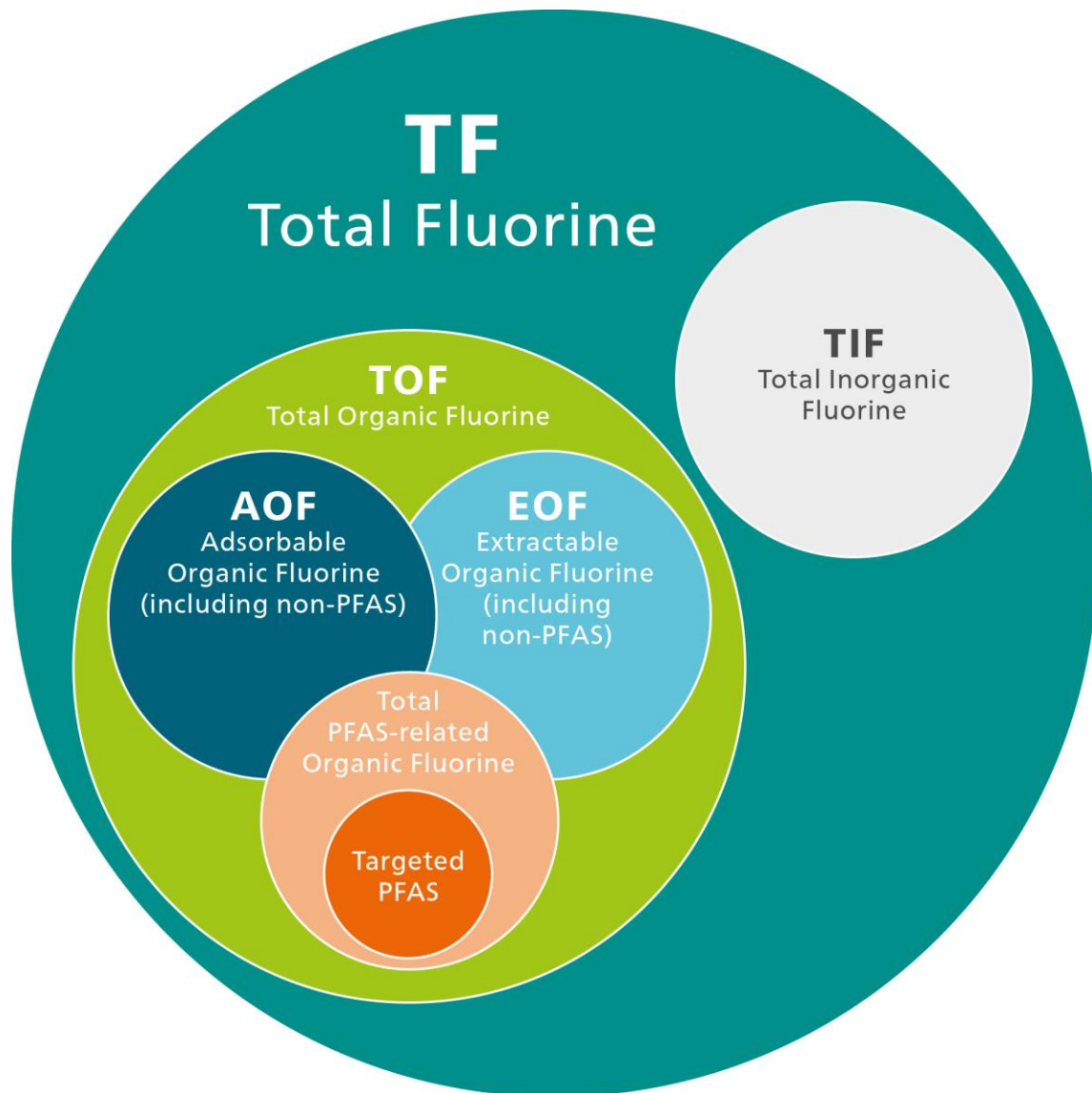
- Adsorption efficiency of Hydrophilic Compounds
- Competing Organic Compounds
- Logistics issues for carbon tube supplies and controlling Fluoride background in adsorption material

EOF Technique:

- Ion Exchange SPE cartridges capacity
- Competing Ions for WAX/SCX/SAX SPEs
- Use of solvents for CIC – Risk of flammability



Classification of Fluorine Compounds

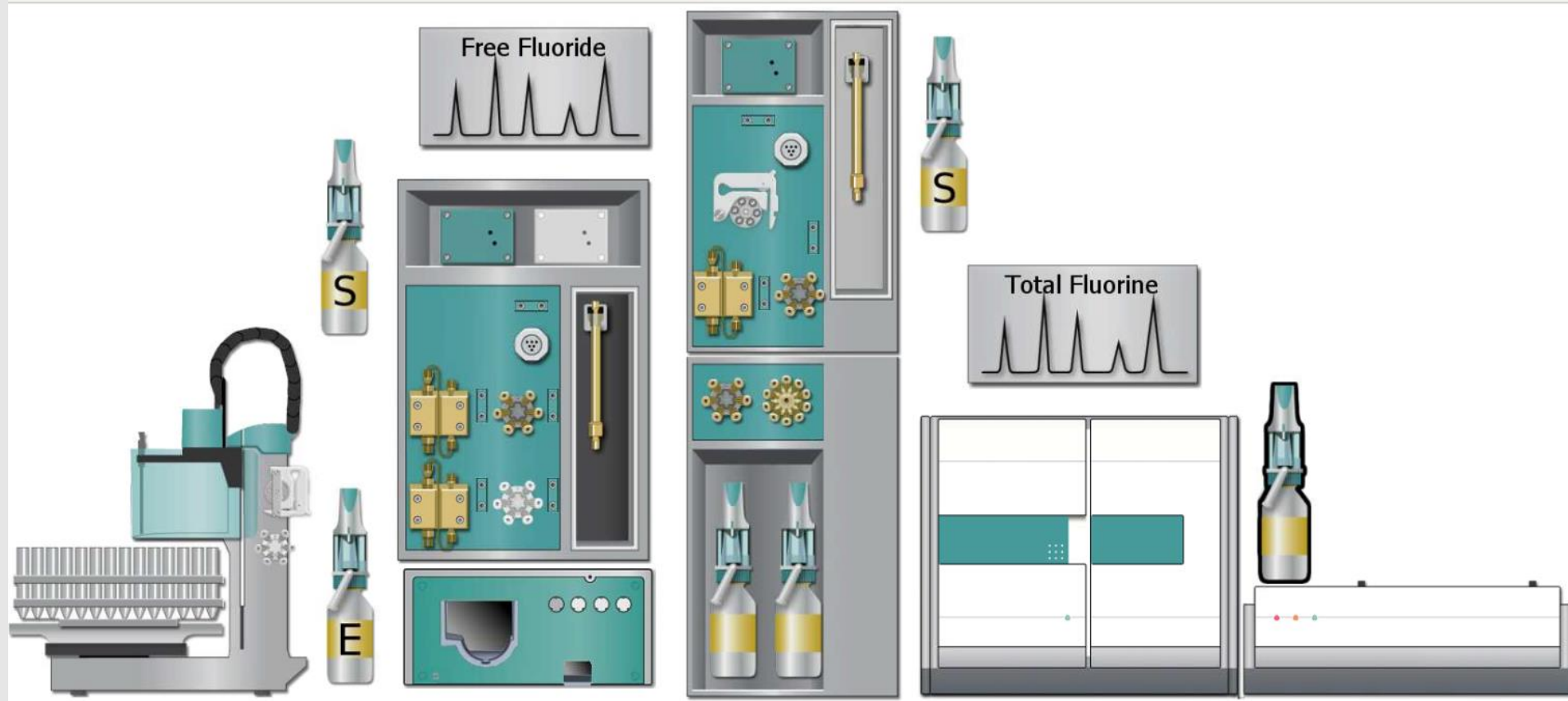




- So based on outlined facts regarding Total Organic Fluorine and limitations of AOF/EOF techniques....
- It is my pleasure to introduce an innovative technique for wastewater samples, which is advantageous because:
 - It is a direct injection of aqueous samples into CIC
 - Elimination of Inorganic Fluoride interference by simple sample prep.
 - It has capability to remove or significantly reduce other interfering inorganic anions and cations
 - This technique ultimately provides trace level analysis of any C1 + Fluorochemicals in Aqueous Samples



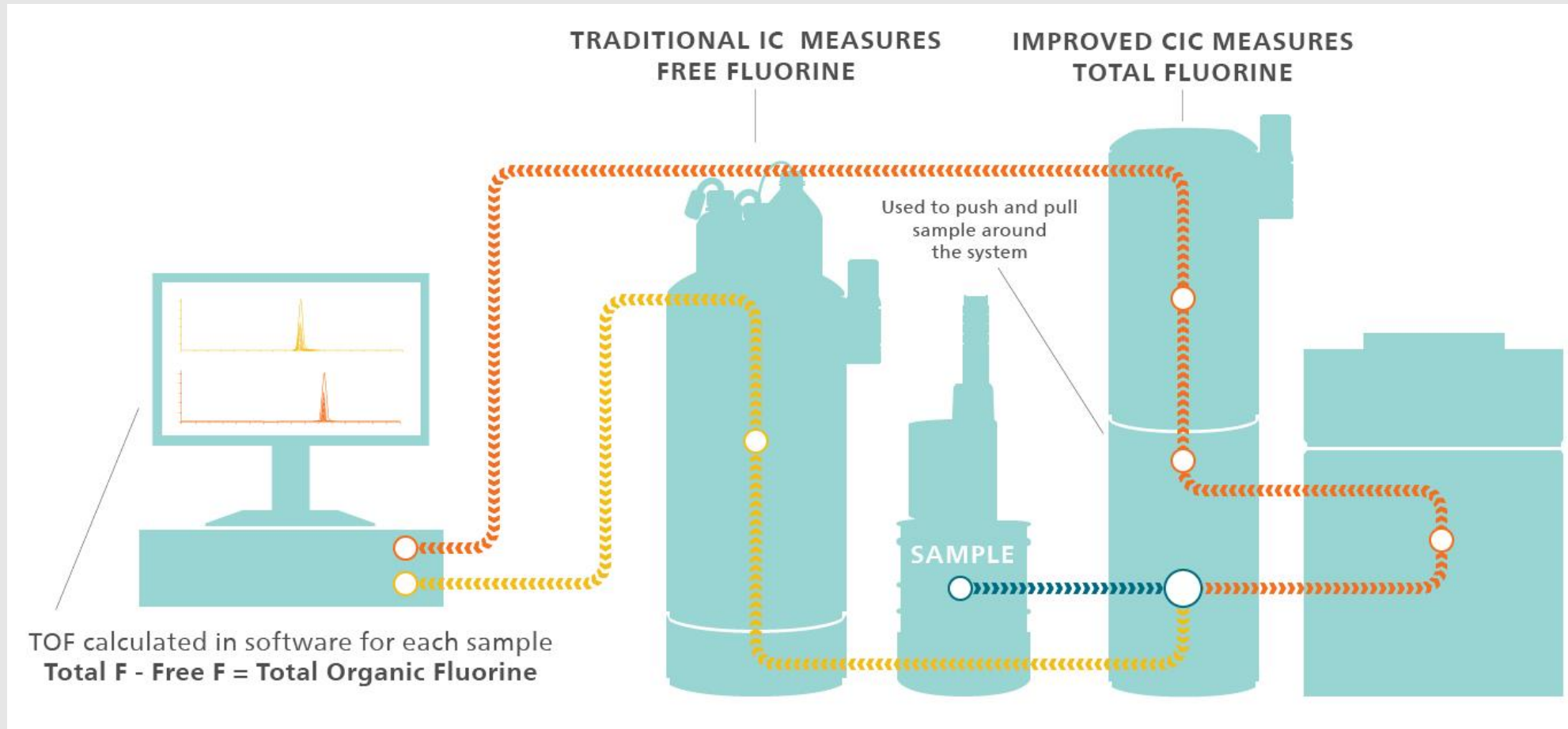
Direct Inject Aqueous Configuration



Screen Shot of instrument method

How it Works

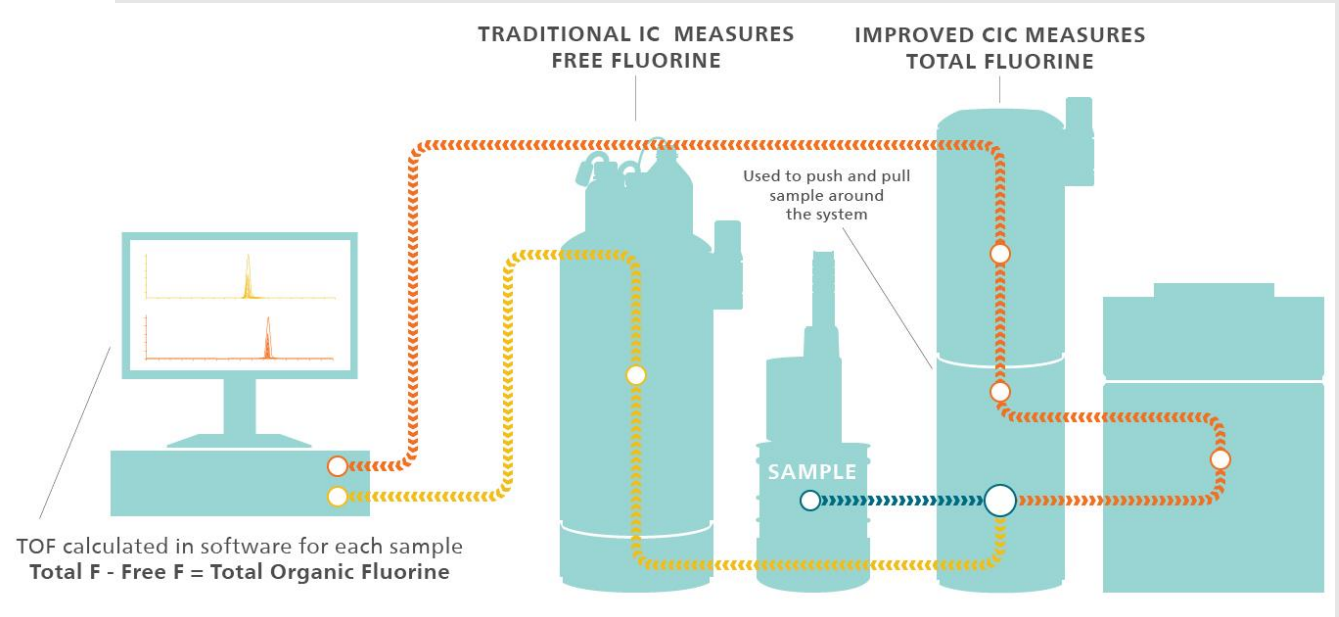
The system takes a single liquid sample and completes both a free fluoride analysis using direct IC and a total fluoride analysis incorporating innovative combustion technology.



$$\text{Total Fluorine} = \text{Total Organic Fluoride} + \text{Free Fluorine}$$

Understanding the needs of trace level TOF analysis

- **Typical Tap Water in USA is Fluorinated from 0.5 ppm to 4 ppm**
 - 0.5 ppm = 500 ppb
 - 4 ppm = 4000 ppb
- **This water ends up in wastewater containing IF**
- **To determine 10 ppb or less TOF in this matrix requires removal of Inorganic Fluoride**

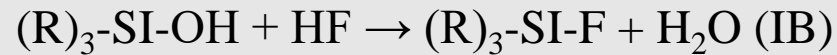
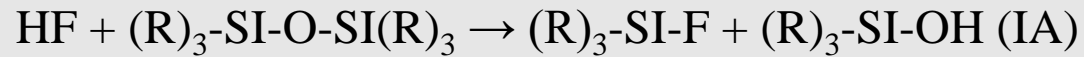


Total Fluorine = Total Organic Fluoride + Free Fluorine

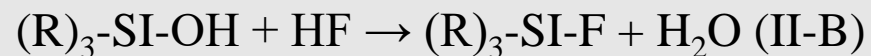
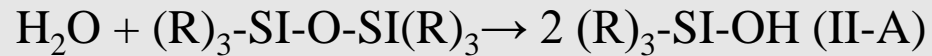
Free Fluoride removal mechanism

METHODS OF REMOVING INORGANIC FLUORIDE FROM COMPOSITIONS CONTAINING FLUORINATED ORGANIC COMPOUNDS

Mechanism I:



Mechanism II:



R = ALKYL GROUPS

Sample Preparation Workflow



Vendors such as Genevac,
Buchi etc.



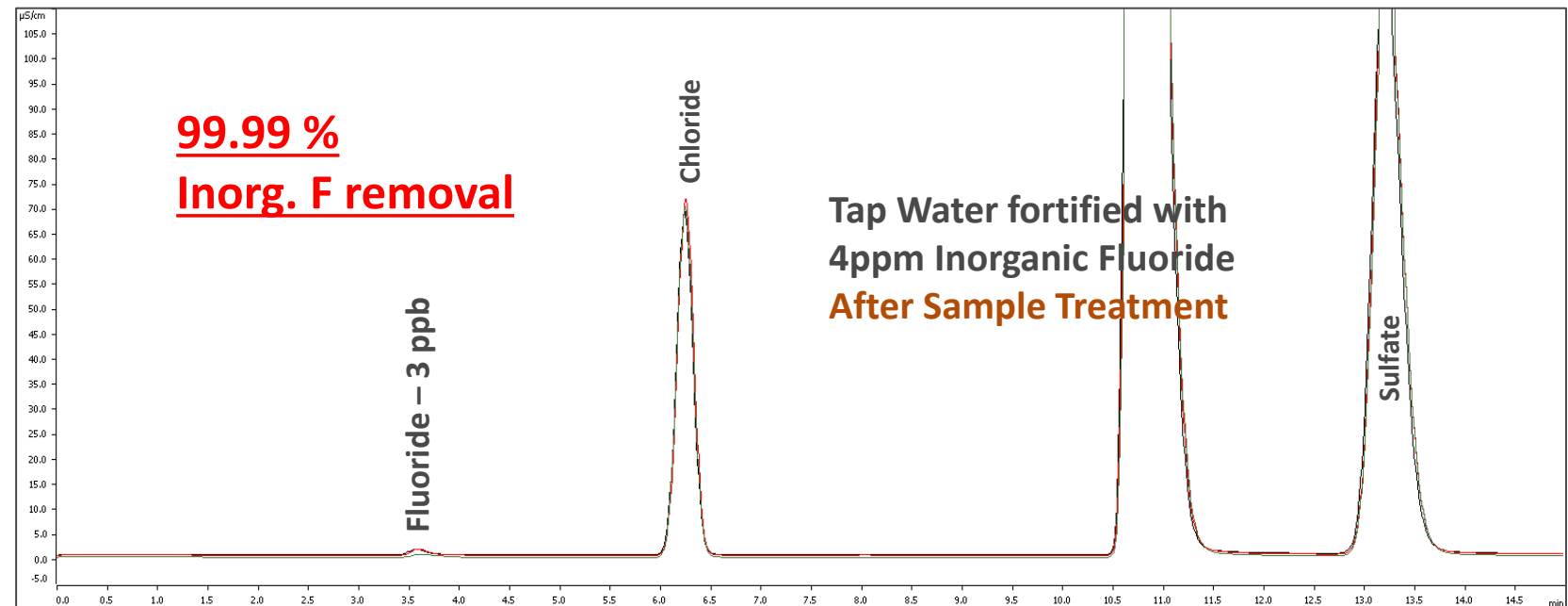
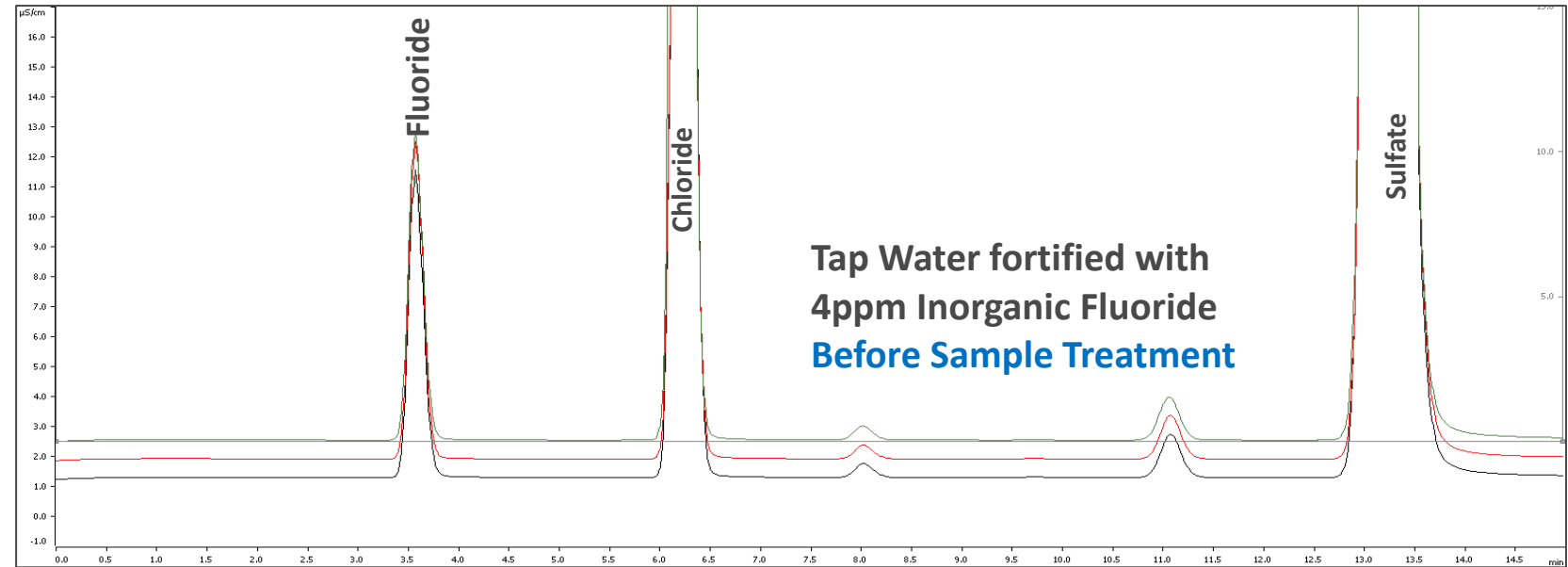
Note: Mostly, tested 1:1 concentration factor for sample up to 10ppm IF removal

Direct Aqueous Inject (CIC) Exemplary Data

- Inorganic Fluoride removal Study in Tampa Tap Water
- Calibration
- Precision and Recovery of spiked Org. F in 0.5 to 4 ppm Fortified Tap Water

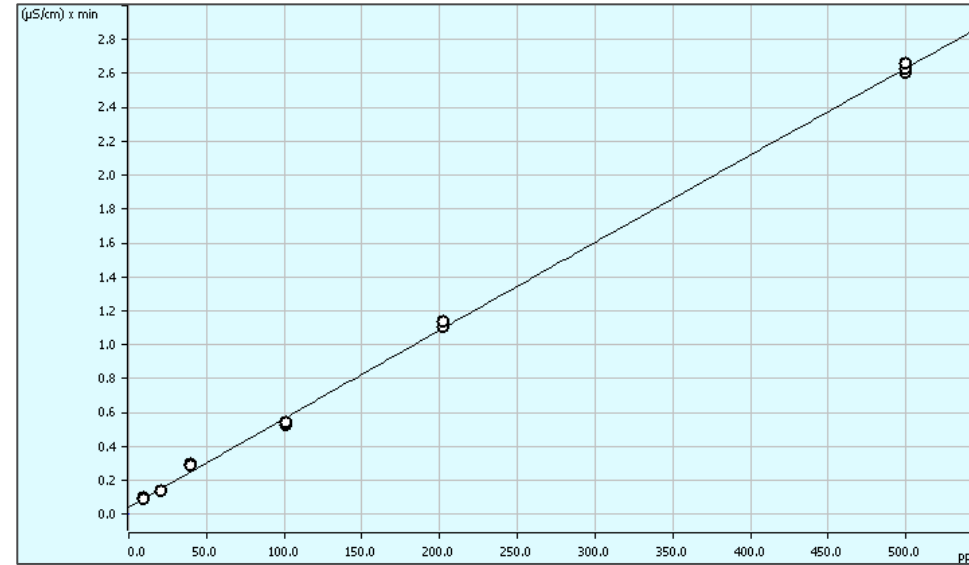


Inorganic Fluoride Removal Study (Tap Water)



- Fortified Tap Water - untreated
- 10 ppb F (from C1+C2+C3 PFC) Spike in fortified Tap Water – after Inorg. F removal
- n = 3

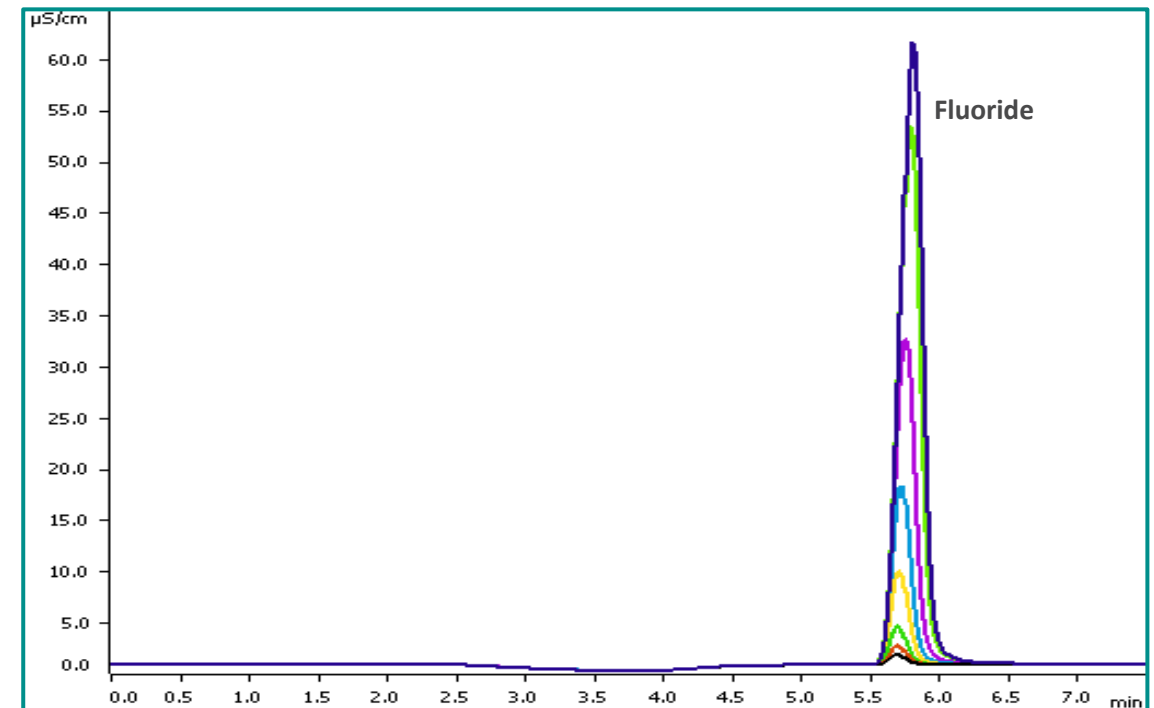
Calibration Direct injection CIC



Relative standard deviation	4.322%
Correlation coefficient	0.999620
Curve type	Quadratic
Weighting	1/Concentration

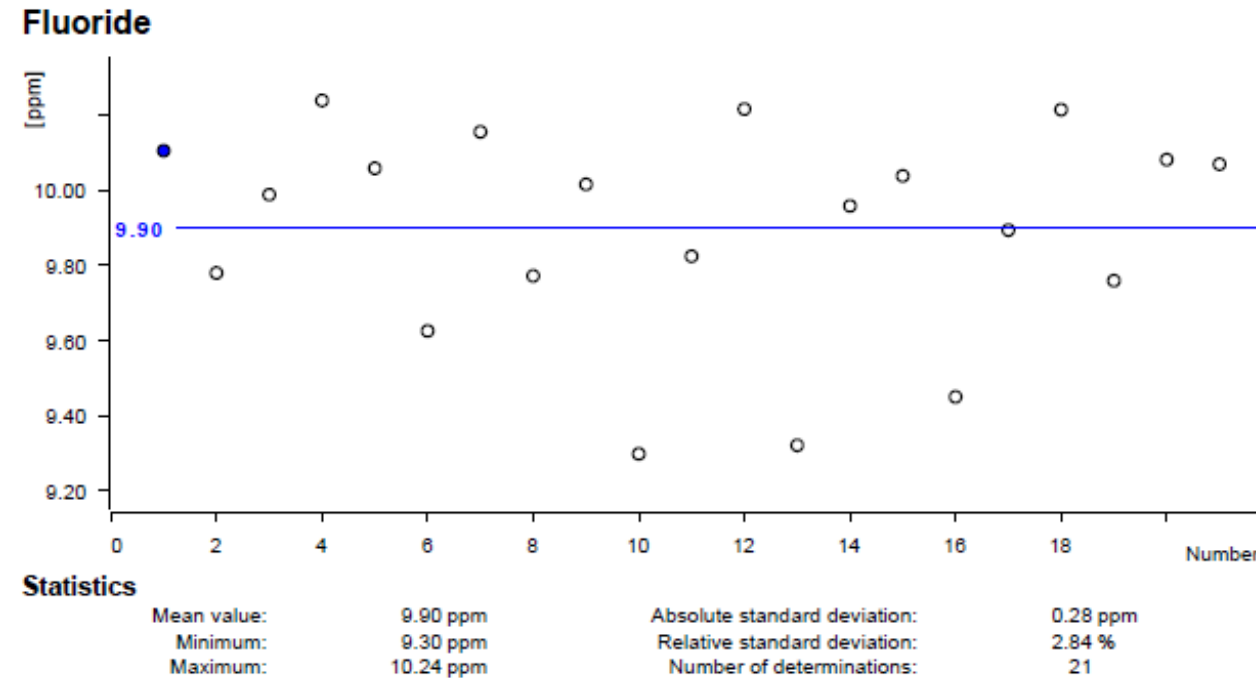
- Range: 5 to 50 ppb F
- Organic F source: C1+C2+C3 PFAS compounds
- # Replicates: n=3

	Equiv. Sample Org. F Conc. (ng/mL)
Std #1	10
Std #2	20
Std #3	40
Std #4	100
Std #5	250
Std #6	500



Check Standards

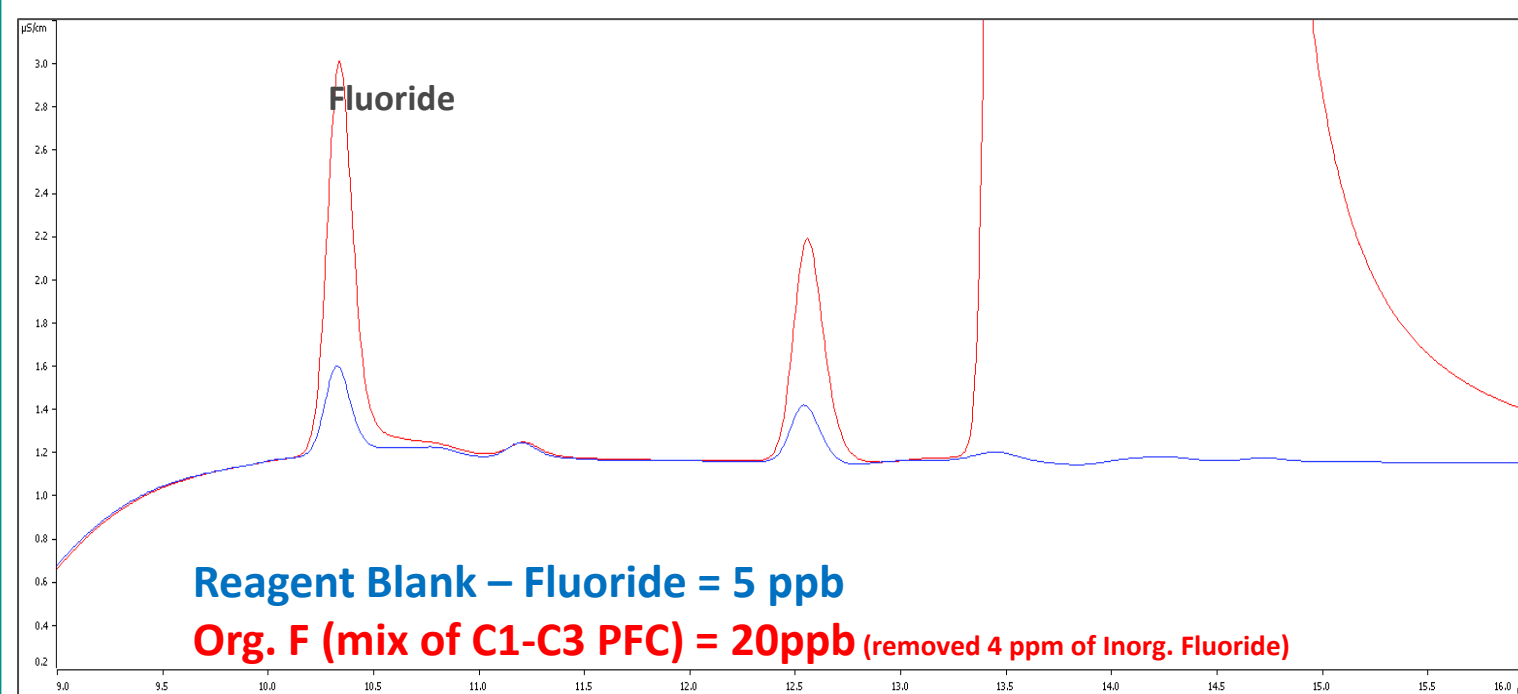
Check Standard (10 ppb F, sample equiv.)



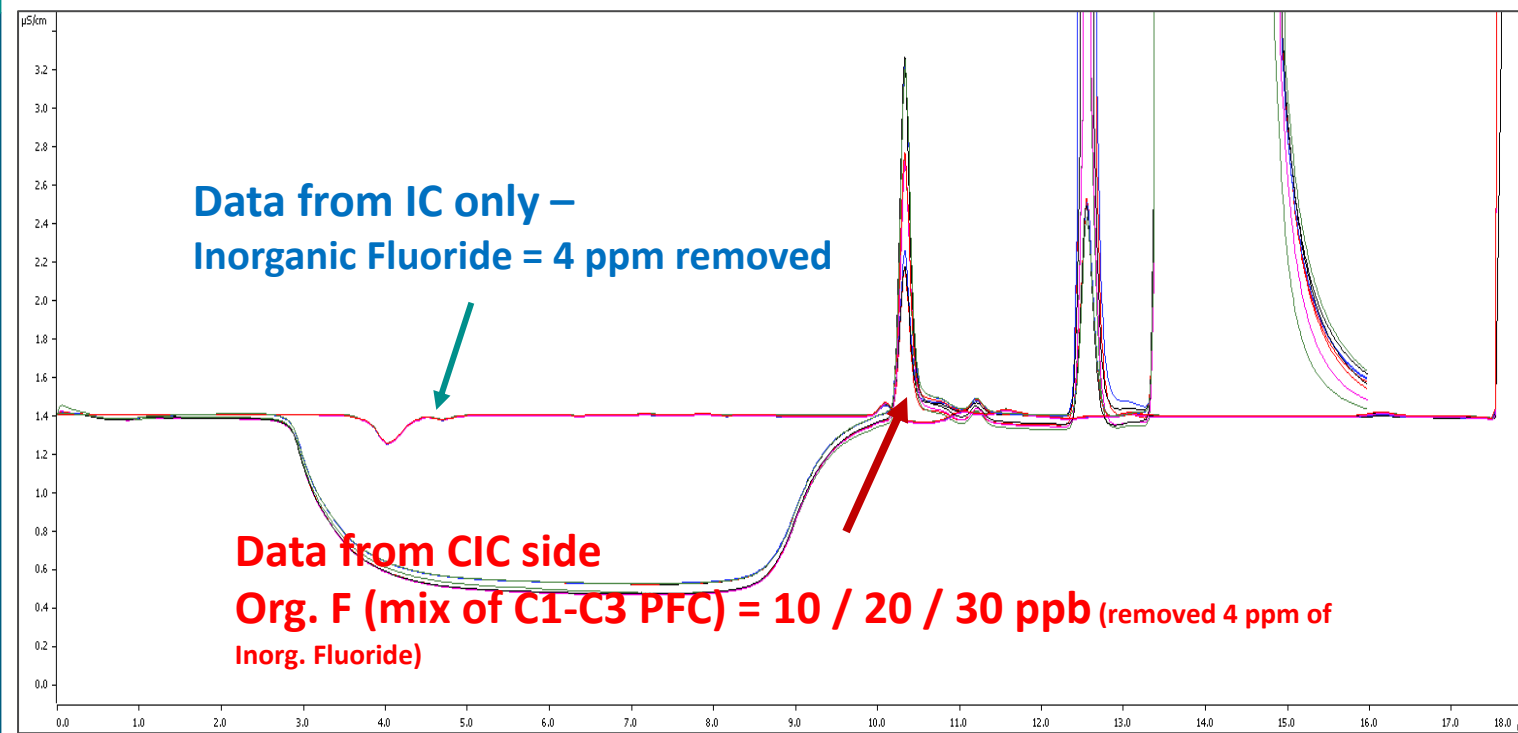
- Check Std : 10 ppb F
- Organic F source: PFBS
- Analyzed between every batch of 10 samples or less

	Avg. Recovery (%)	RSD (%)
Check Std	99.6	2.8

Organic Fluoride Recovery Study (Fortified Tap Water)



- Tap Water fortified with 4ppm Inorganic Fluoride
- Sample preparation workflow to remove Inorganic F
- Organic F = 10 / 20 / 30ppb



Profiler-F for Wastewater – Next Steps

Profiler-F for Wastewater

- Evaluation of real-world wastewater samples – work in progress
- Optimizing the sample prep to “concentrate” the sample to achieve sub-ppb level detection



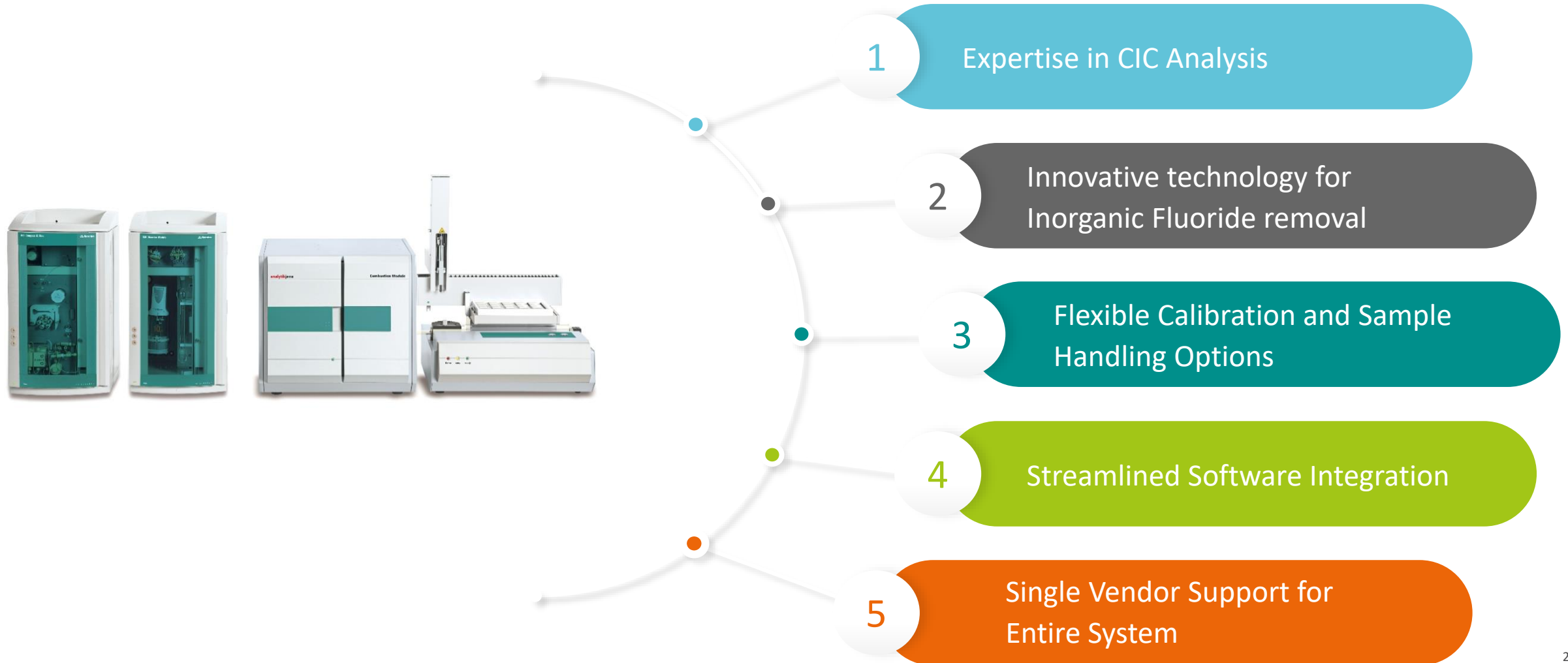
Innovative Technology For Direct inject CIC

Profiler-F for Wastewater

- Metrohm just introduced Innovative technology to remove Inorganic Fluoride
- Direct injection of wastewater samples for TF analysis
- This technique will allow analysis of Total Fluorine from Fluorochemicals from C₁ – C_n (all water-soluble compounds)
- Parts per billion (ppb) detection levels achieved



Metrohm CIC Advantages



Thank You



Questions? Please contact us at communications@metrohmusa.com