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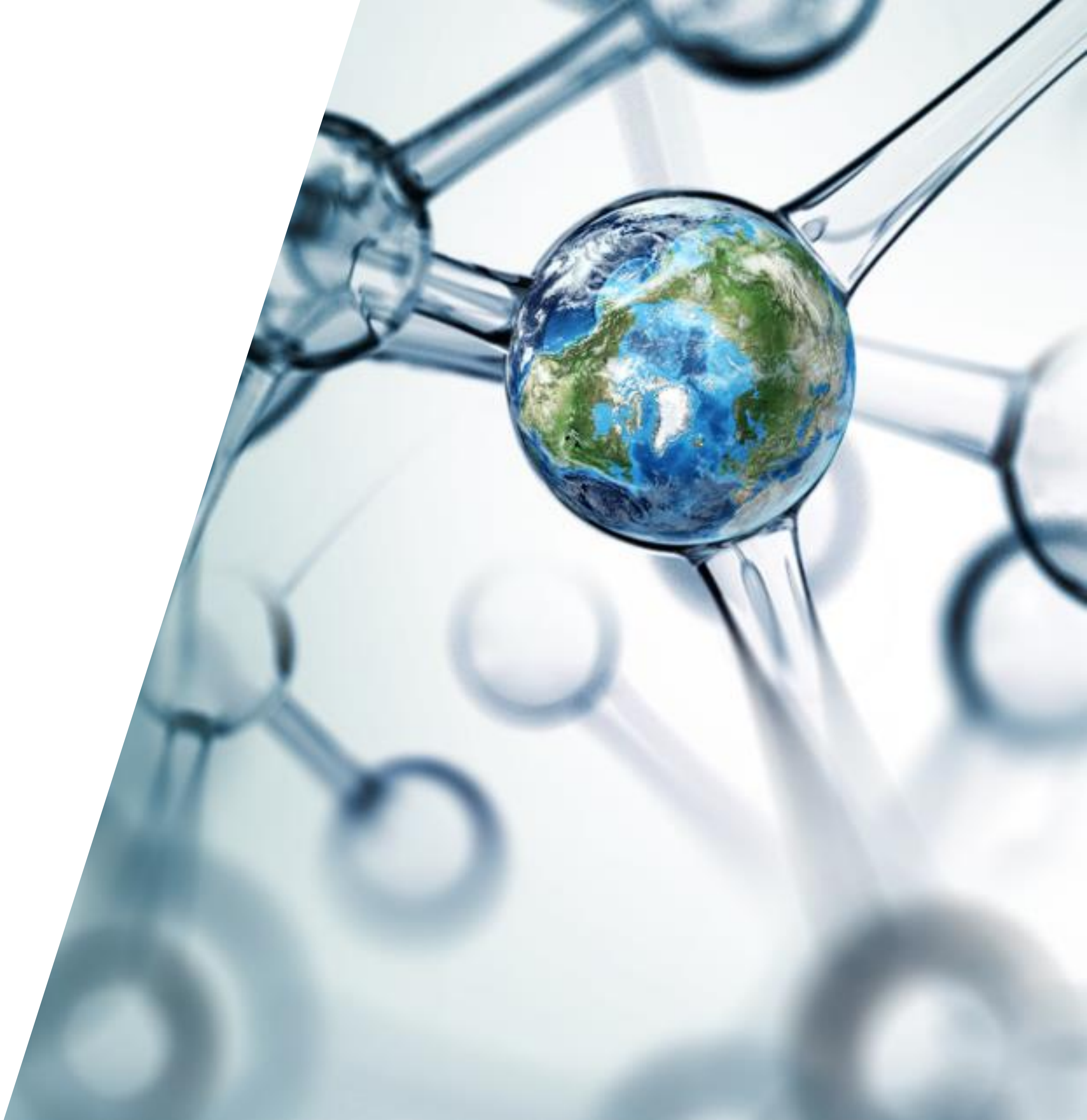
Determination of total PFAS in Food-Contact Materials (FCM) using Combustion Ion Chromatography (CIC)

Chris Shevlin and Jingli Hu
Scientific and Regulatory Affairs Manager

August 8, 2024

EMS 2024



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Food packaging environmental impact

https://toxicfreefuture.org/federal-policy/pfas-in-food-packaging/

Sources and actions

Where PFAS is found:

- Non-stick frying pans, baking and roasting pans
- Fast food wrappers, pizza boxes and microwave popcorn bags
- Paper based products like plates, cups and straws
- Plastic food packaging from grocery stores
- Food processing equipment

Not always intentionally added or manufacturers are unaware of PFAS presence

Taking action:

- Some states are banning intentionally used PFAS
- Other states are placing limits on total organic fluorine (i.e. 50 to 100 ppm)
- FDA voluntary phase-out program
- EPA has declared PFOA and PFOS as hazardous substances under CERCLA
- EU is proposing a total PFAS ban

Good monitoring and reliable methods are crucial. No standardized methods are available.

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State restrictions on PFAS

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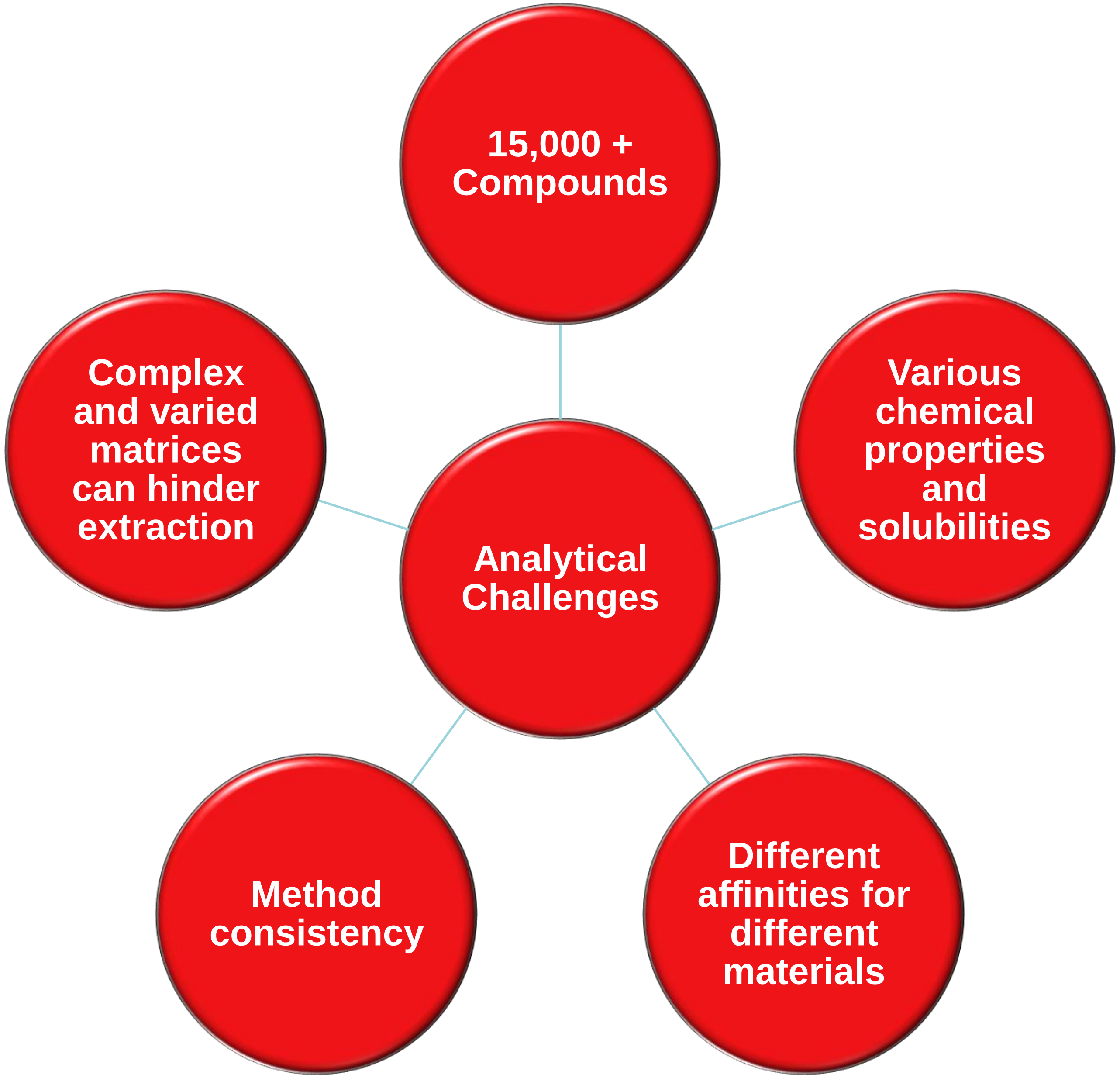
Class-based PFAS phase-outs in key sectors with implementation years

	All Products	Apparel	Carpets / Rugs	Cleaning Products	Cookware	Dental Floss	Fabric Treatments	Firefighting Foam	Food Packaging	Juvenile Products	Menstrual Products	Oil & Gas Products	Personal Care Products	Pesticides	Ski Wax	Sludge (biosolids)	Textile Articles
California		★ 2025	2021**				2022**	2022	2023	2023			2025				★ 2025
Colorado		2028	2024	2026	2026	2026	2024	2024	2024	2024	2026	★ 2024	★ 2025		2026		2028
Connecticut								2021	2023								
Hawaii								2024	2024								
Illinois								2025									
Maine	2032	2029	2023	2026	2026	2026	2023	2022	2022	2026	2026		2026	★ 2030	2026	★ 2022	2026
Maryland			2024					2024	2024				2025*				
Minnesota	2032		2025	★2025	★ 2025	★ 2025	2025	2024	2024	2025	★ 2025		2025		2025		2025
New Hampshire								2020									
New Jersey								2026									
New York		2025	2024					2020	2022								
Oregon									2025	2023**			2027				
Rhode Island									2024								
Vermont		2028	★ 2023		2026		★ 2023	2023	2023	2026	2026		2026		★2023		2026
Washington	★ 2023**		2023				2023	★ 2020	★ 2022				2025				2023
Totals	**3**	**5**	**8**	**3**	**4**	**3**	**6**	**13**	**12**	**6**	**4**	**1**	**8**	**1**	**4**	**1**	**6**

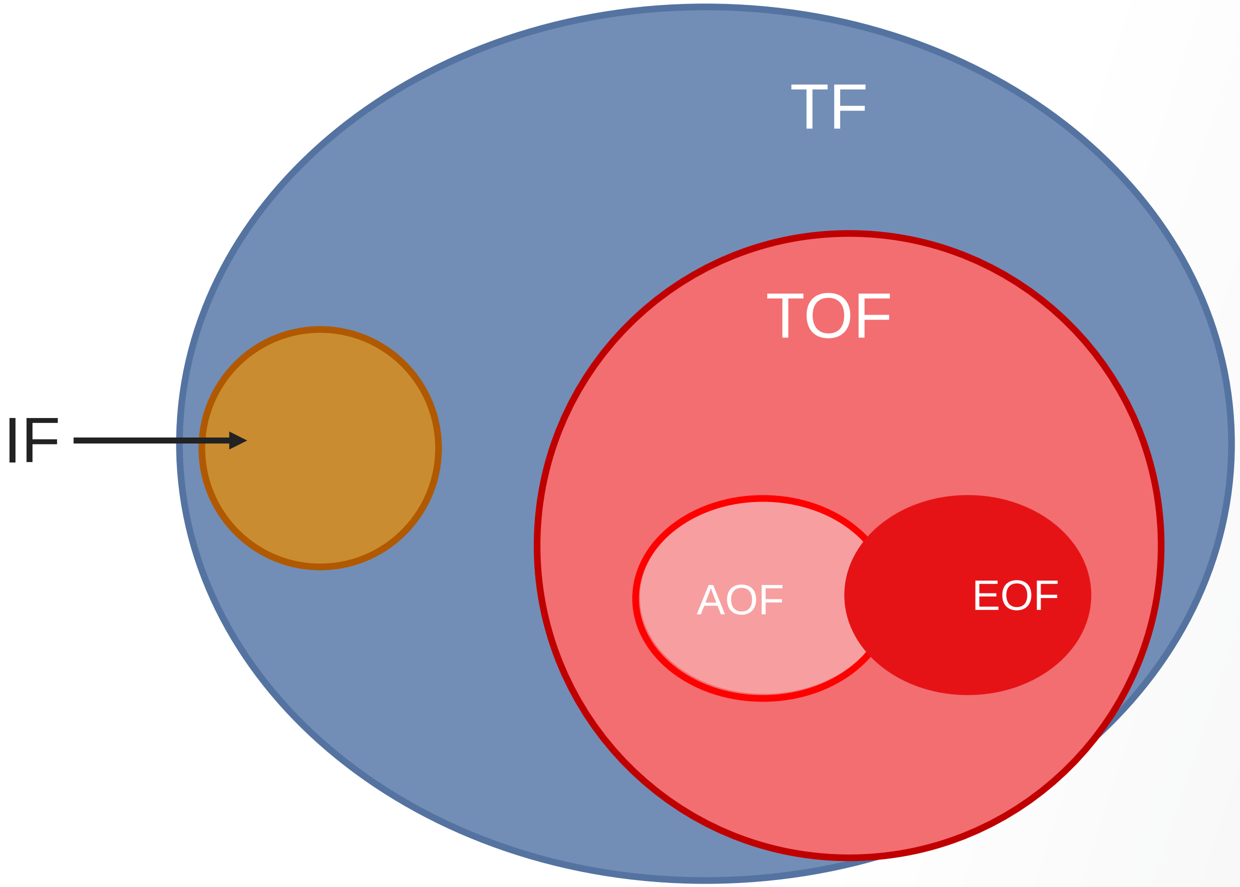
https://www.saferstates.org/priorities/pfas/

* not class-based; covers some PFAS substances but not all
** ongoing regulation
★ indicates the state was the first to adopt policy banning PFAS in that specified key sector

Challenges to determining total PFAS



Total fluorine mass balance determination



TF = Total Fluorine

IF = Inorganic F

TOF = Total Organic F

AOF = Adsorbable OF

EOF = Extractable OF

Addressing the challenge – which method?

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What is the best approach to determining total PFAS

Total Fluorine

- Good indicator of a sum parameter for fluorine
- Simplified Method
- Need to account for possible inorganic fluorine

Direct combustion alone may not be accurate

Extractable Organic Fluorine

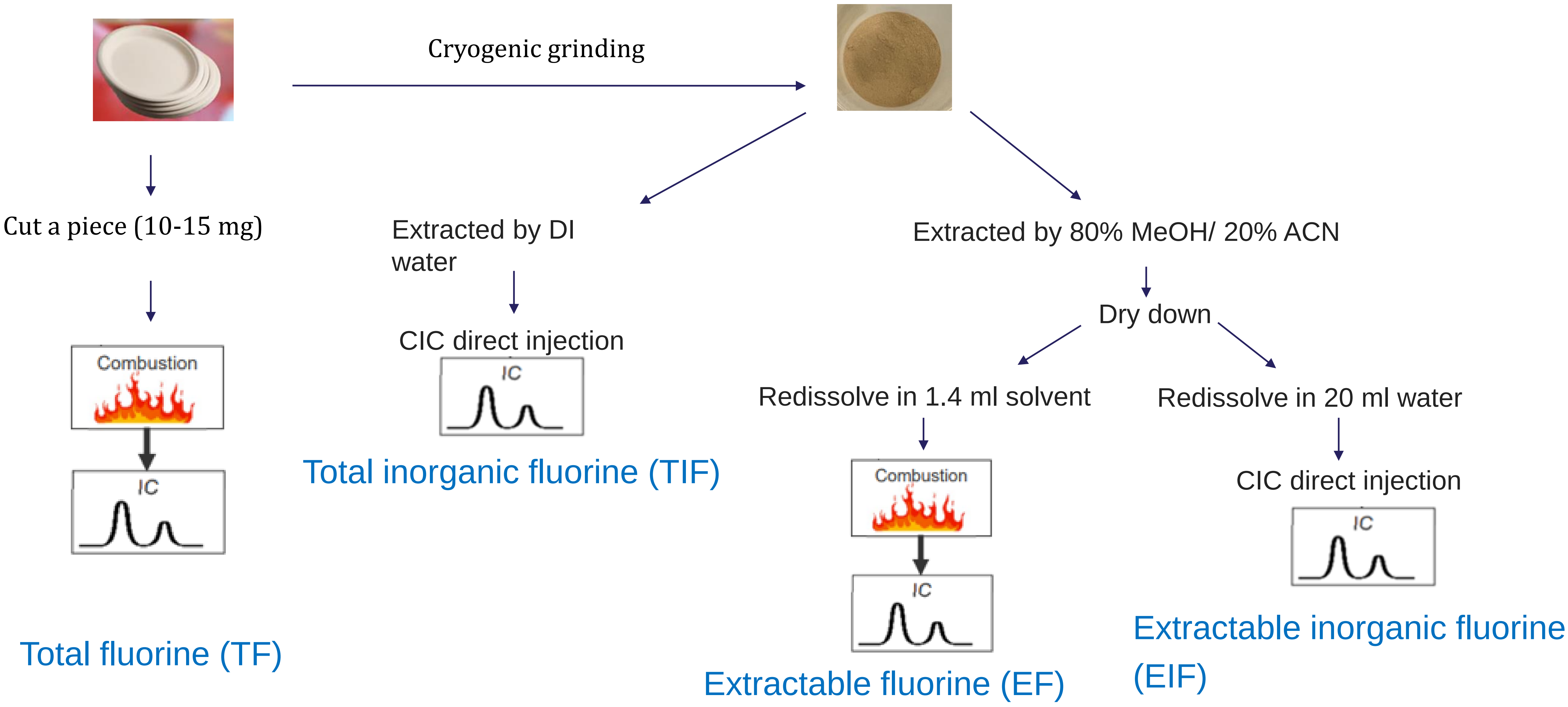
- Selective for organic fluorine
- Amenable to compound ID and provides a mass balance target
- Some PFAS are not extractable; fluoropolymers

May not be comprehensive of total PFAS

Adsorbable Organic Fluorine

Not a viable option because of the nature of the sample. An extraction would have to be done which would lead to poor adsorption

TOF and EOF analysis flow chart



TOF and EOF analysis procedure

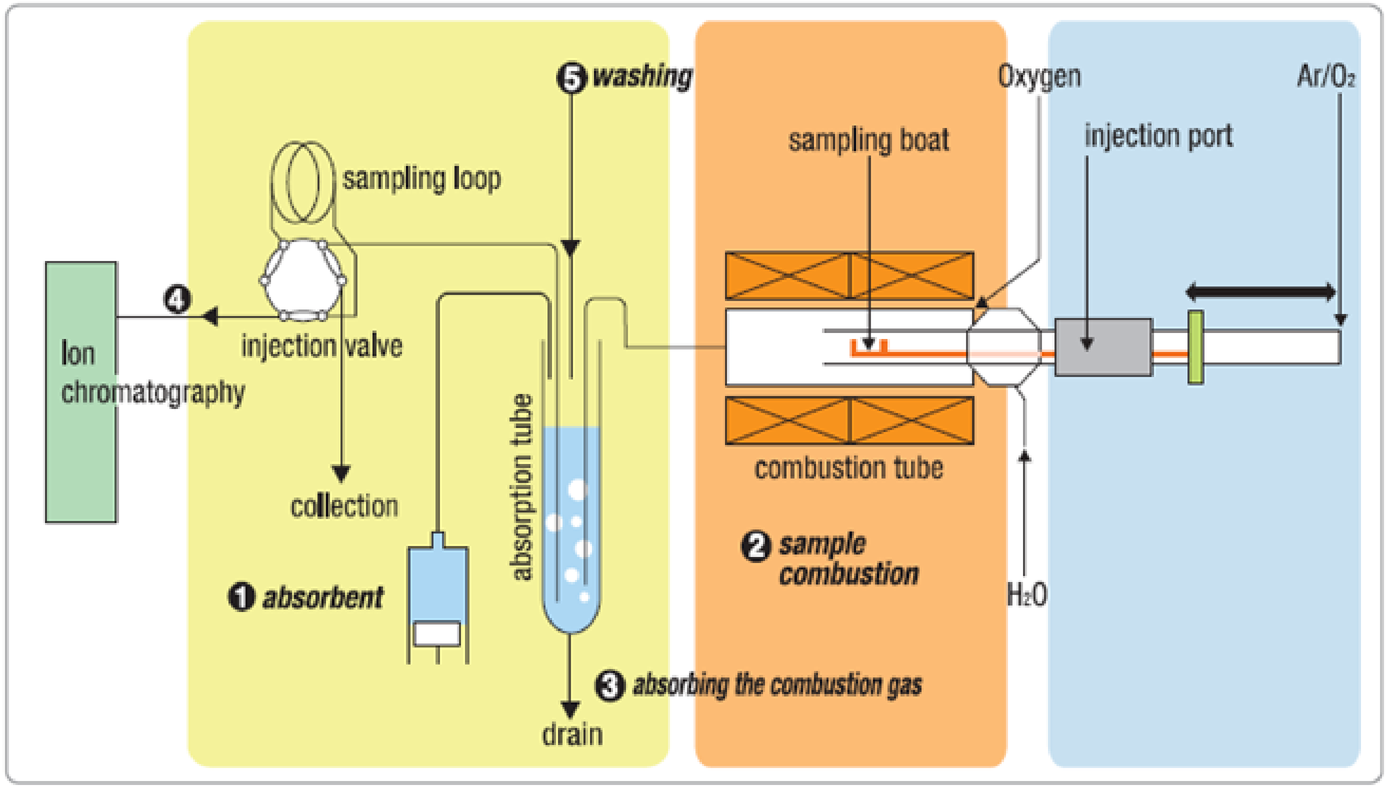
Samples

- Heavy duty disposable bowl
- Bakery paper sandwich bag
- Compostable disposable paper plate

Direct Combustion Sample Prep:

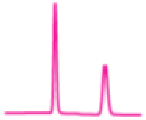
1. 1g of ground sample in a 50 mL centrifuge tube
2. Add 20 mL DI Water and sonicate for 10 min
3. Centrifuge for 10 min @ 15,000 g
4. Collect supernatant and filter with a PES filter into a 15 mL vial
5. Place a portion on the CIC system

Combustion IC schematic



Process Flowchart

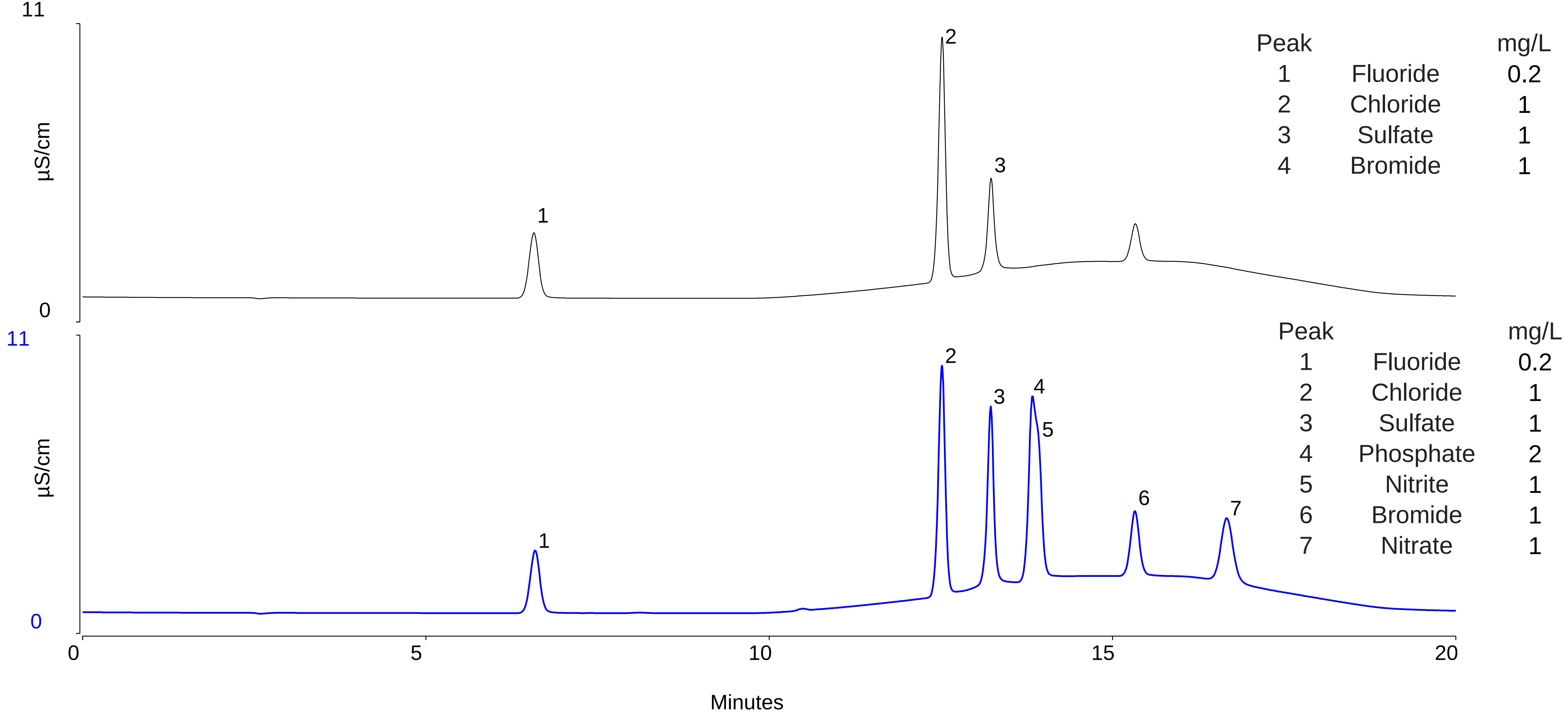
1. set absorbent
2. pyrohydrolytic combustion of sample
3. combusted gas is absorbed by absorbent
4. absorbent is injected into the Ion chromatograph
5. clean absorption tube

Sample	→	Combustion Tube	→	Absorption Solution	→	IC System
Organic sulfur	→	SO_x	→	SO_4^{2-}	→	
Inorganic halogen	→	HX, X_2	→	X^-	→	

Combustion IC Conditions

Chromatographic Conditions Combustion and IC	
Columns	Dionex IonPac AG24-Guard Column, 2 x 50 mm Dionex IonPac AS24-Analytical Column, 2 x 250 mm
Eluent	8 mM KOH from 0-6 min, 8-75 mM KOH from 6-10.25 min, 75 mM KOH from 10.25-12 min, 75-8 mM KOH from 12-15 min, 8 mM KOH from 15-20 min
Eluent source	Dionex EGC 500 KOH with Dionex CR-ATC 600
Flow rate	0.3 mL/min
Column temperature	30 °C
Injection volume	25 µL
Detection	Suppressed Conductivity, Dionex ADRS 600 Suppressor (2 mm)
Furnace temperature	950 ° C inlet, 1000 ° C outlet
Gas	Ar: 200 mL/min; O2: 400 mL/min
Hydration	Water/Ar: 100 mL/min
Boat Program	Position / Wait time (s) / Speed (mm/s) 90 mm / 60 / 10 End / 600 / 10 Cool / 60 / 40 Home / 120 / 20
Run time	20 min

Seven anion separation

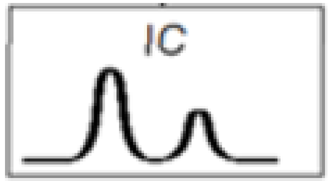


Consistent fluoride results between direct and combustion injection

Inorganic fluorine

Cryogenic grind

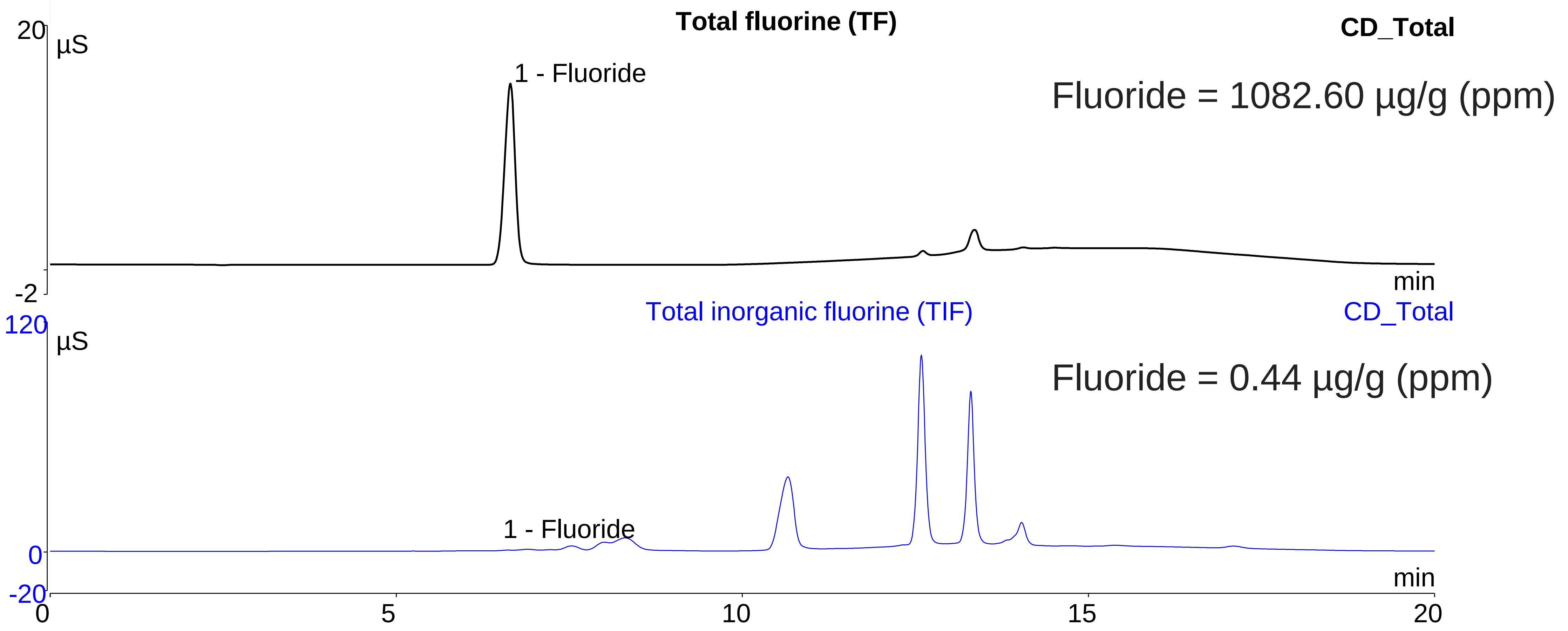
Extracted by DI water



CIC direct injection

Total inorganic fluorine (TIF)

Total organic fluorine (TOF) determination



TF – TIF = Total organic fluorine

1082.60 - 0.44 = 1082.16 µg/g (ppm)

Extractable organic fluorine

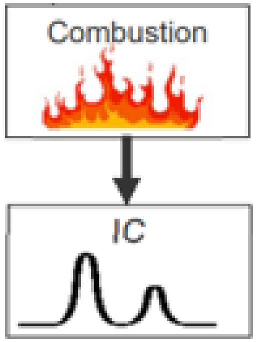
Cryogenic grind

Extract 80:20 MeOH/MeCN by Gas-Assisted Accelerated Solvent Extraction

Evaporate to dryness

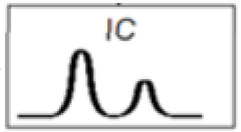
EOF

Recon in 80:20 MeOH/MeCN



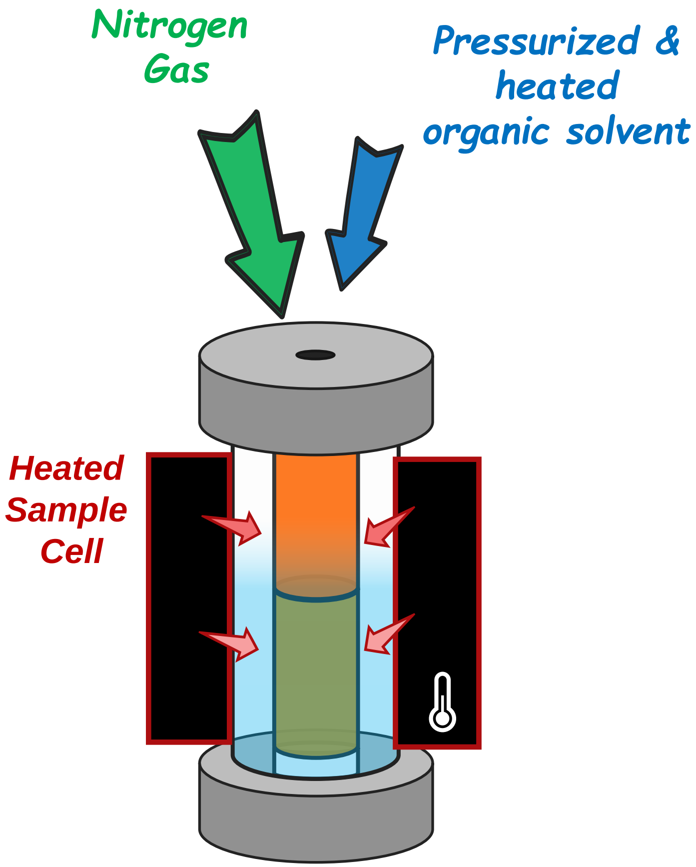
EIF

Recon in 20 mL DI Water



CIC direct injection

A closer look at extraction



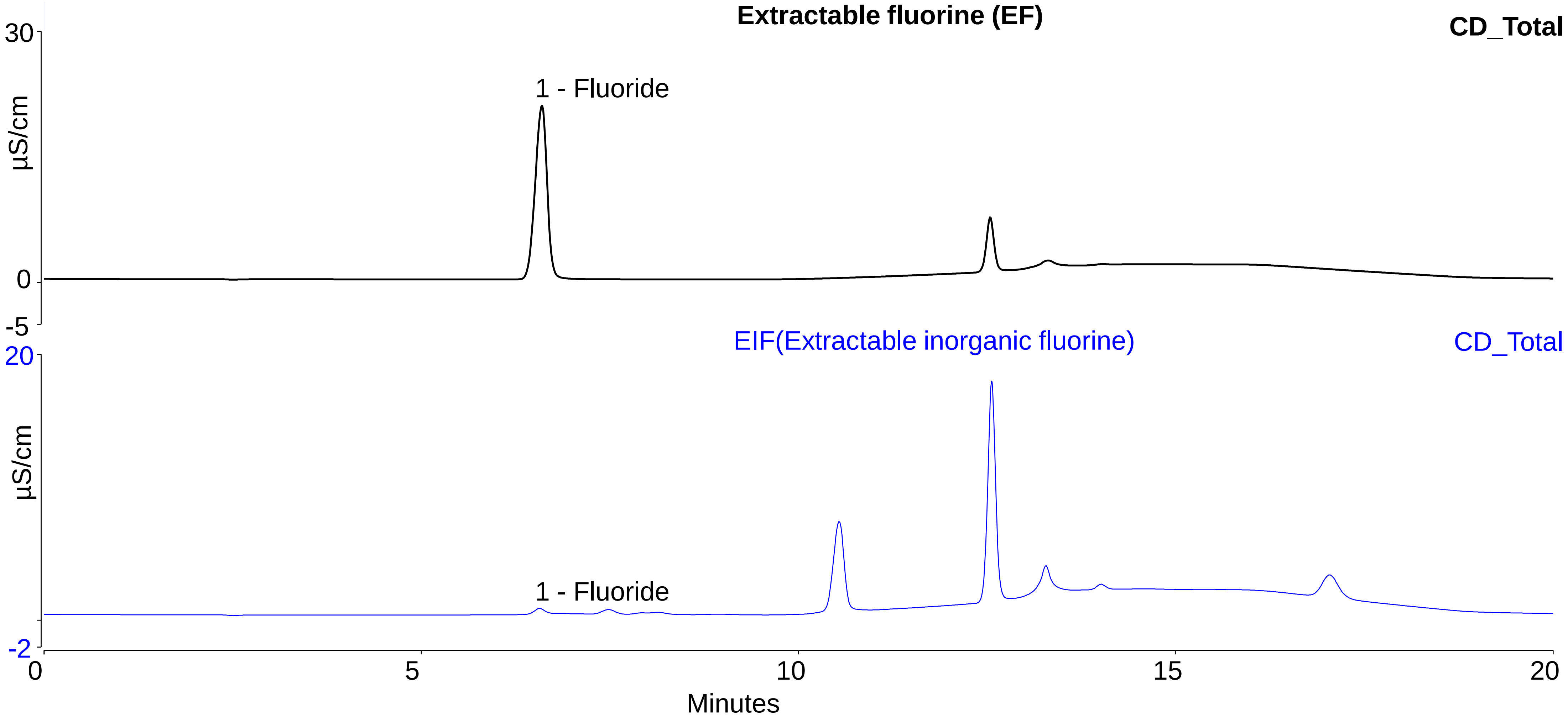
Thermo Scientific™ EXTREVA™
ASE™ Accelerated Solvent Extractor

Sample Prep Steps

1. 1g ground sample into a 10 mL ASE cell
2. Extract with 80:20 MeOH/MeCN at 60ºC for 15 min at 1 mL/min; N_2 gas flow 10 mL/min – Cell pre-fill volume at 50%
3. Purge the cell for 45 sec

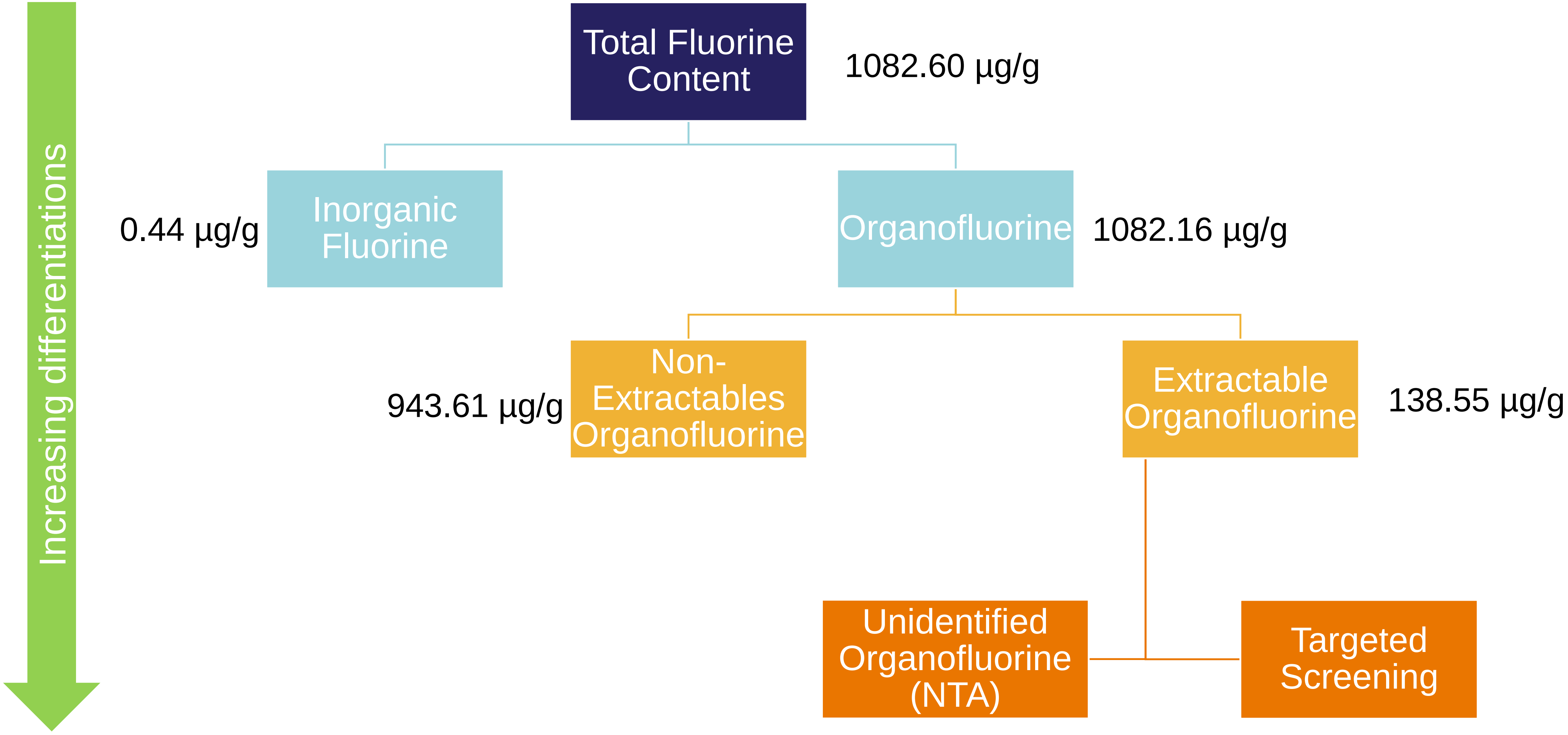
Four samples are extracted in parallel
16 samples take just over an hour

EOF results accounting for extractable inorganic F$^-$



EOF = 138.55 µg/g (ppm)

Total fluorine mass balance



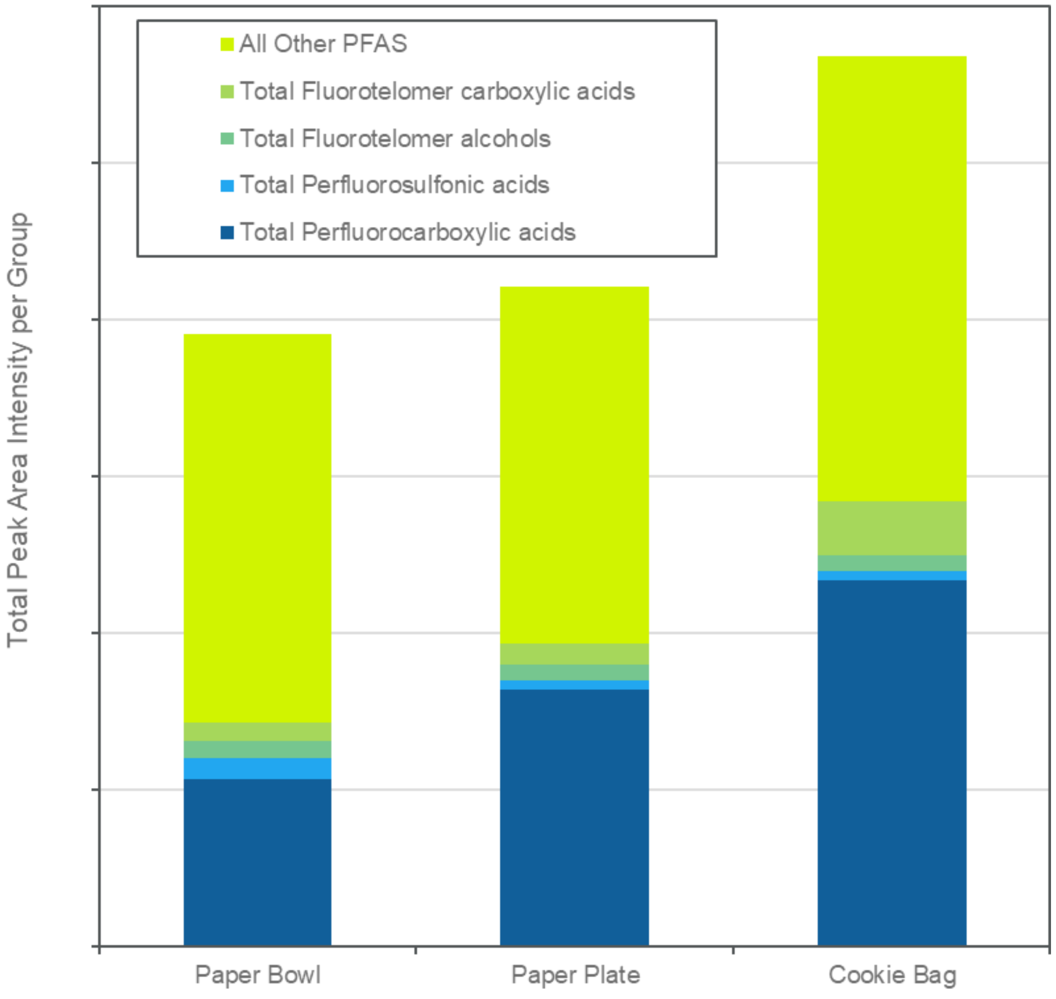
Sample results

Sample	TF	TIF	TOF(TF-TIF)	EF	EIF	EOF (EF-EIF)	EOF/TOF (%)
1	1082.60	0.44	1082.16	139.02	0.47	138.55	12.8
2	1369.21	0.32	1368.89	90.33	0.29	90.03	6.6
3	2141.97	0.21	2141.76	72.82	0.22	72.60	3.4

TOF and EOF in food contact material, ppm (µg/g) (n=3, RSD<6%)

- Many manufacturers have adopted a limit of 100 ppm as measured by TOF
- All TOF results are over the100 ppm threshold, which also violates some current and proposed state limits
- Classification of the compounds found during extraction can give helpful information to the nature of the high PFAS amounts

Nontargeted analysis (NTA) with LC-HRAM



PFAS class determination:

Thermo Scientific™ Orbitrap Exploris™ 240 (Thermo Fisher Scientific) coupled to a Thermo Scientific™ Vanquish™ Flex UHPLC system

Conclusions

- We developed sensitive and automated methods to determine TOF and EOF in FCM using CIC.
- The TOF measurement is a good indicator of a sum PFAS parameter
- The TOF method can be used by manufacturers to comply with current state regulations or internal limits.
- The amount of extractable fluorine is limited in FCM, which suggests that targeted LC-MS approaches miss much of the PFAS content in the samples, such as unidentified EOF compounds and non-extractable OF.

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