Chesapeake Bay Program Toxic Contaminant Workgroup
June 12, 2024

Development of EPA Method 1621: Determination of Adsorbable Organic Fluorine in Aqueous Matrices by Combustion Ion Chromatography

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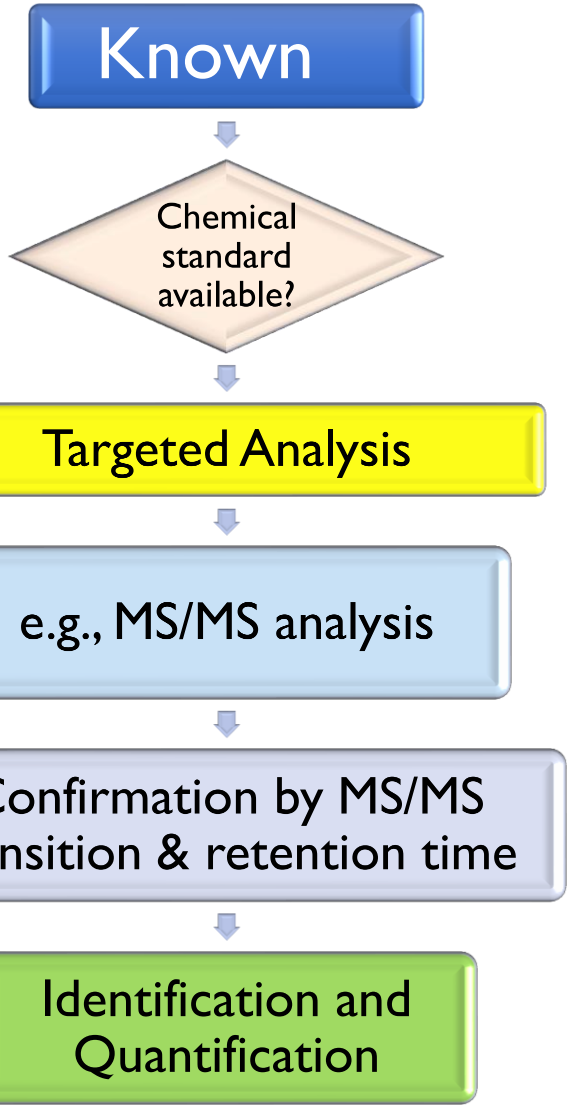
Center for Environmental Solutions and Emergency Response

Target Analysis Background

- Currently, the most common PFAS detection technique is mass spectrometry (LC/MS, LC/MS/MS, HRMS, etc)
  - **Target Analysis:**
    - Methods applicable to a specific defined set of known analytes
    - Analytical standards exist for quantitation
    - Methods only measure for analytes on the targeted list; once the analysis is complete, you can't look for other analytes.


Known

Chemical standard available?

Targeted Analysis

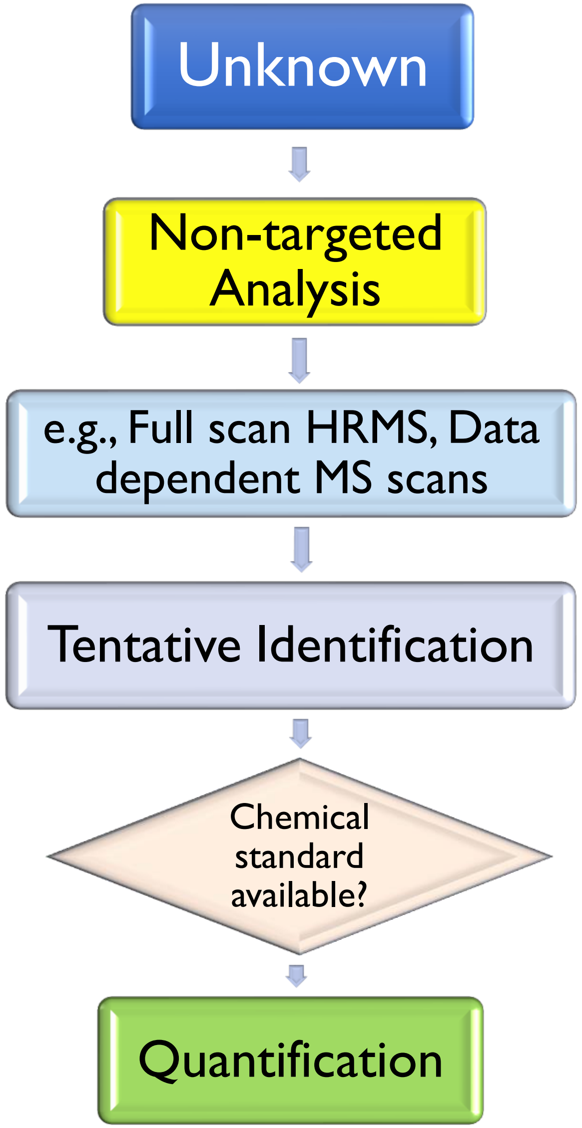
e.g., MS/MS analysis

Confirmation by MS/MS transition & retention time

Identification and Quantification

Non-Target Analysis Background

- **Non-Targeted Analysis:**
  - Methods use high resolution mass spectrometry (HRMS) capable of identifying known & unknown analytes in a sample
  - Can screen for lists of known suspects and discover new or unknown analytes providing a tentative ID
  - HRMS data can be stored and analyzed later for newly identified analytes
  - If standard is available, quantitation can be performed
  - Expensive, long data analysis process, requires advanced MS skill



Unknown

Non-targeted Analysis

e.g., Full scan HRMS, Data dependent MS scans

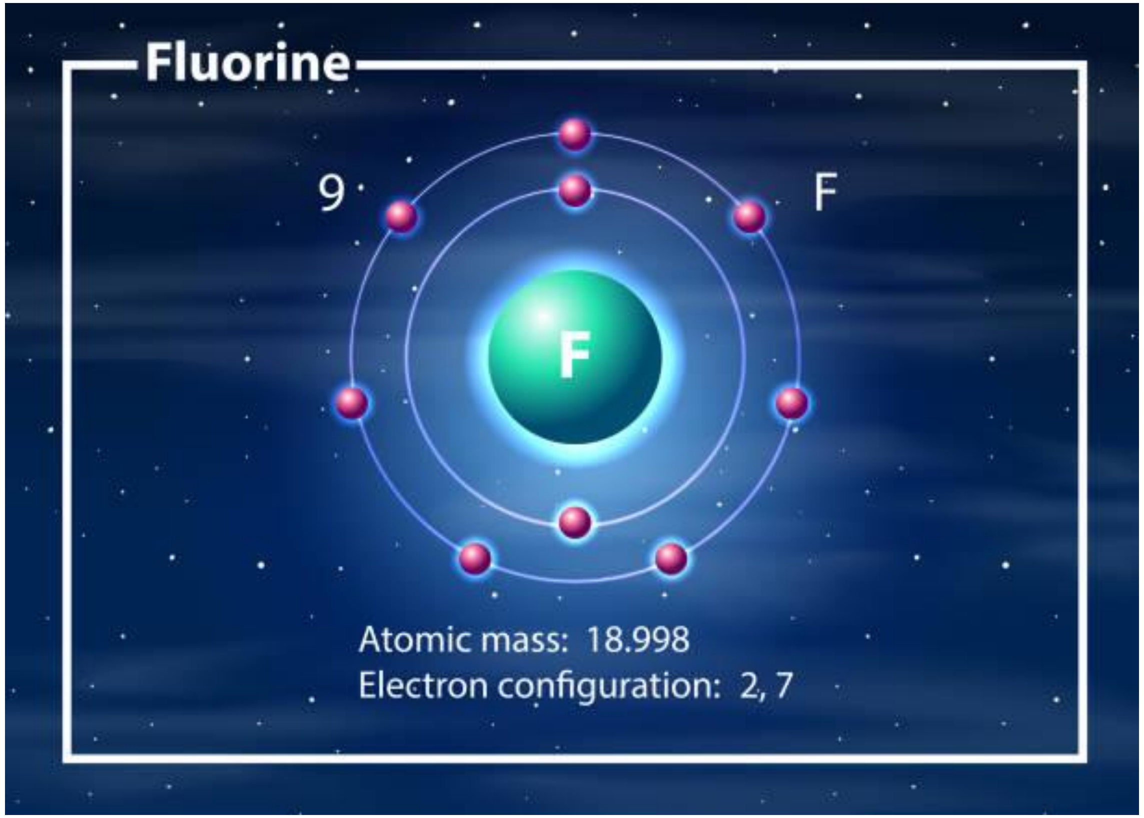
Tentative Identification

Chemical standard available?

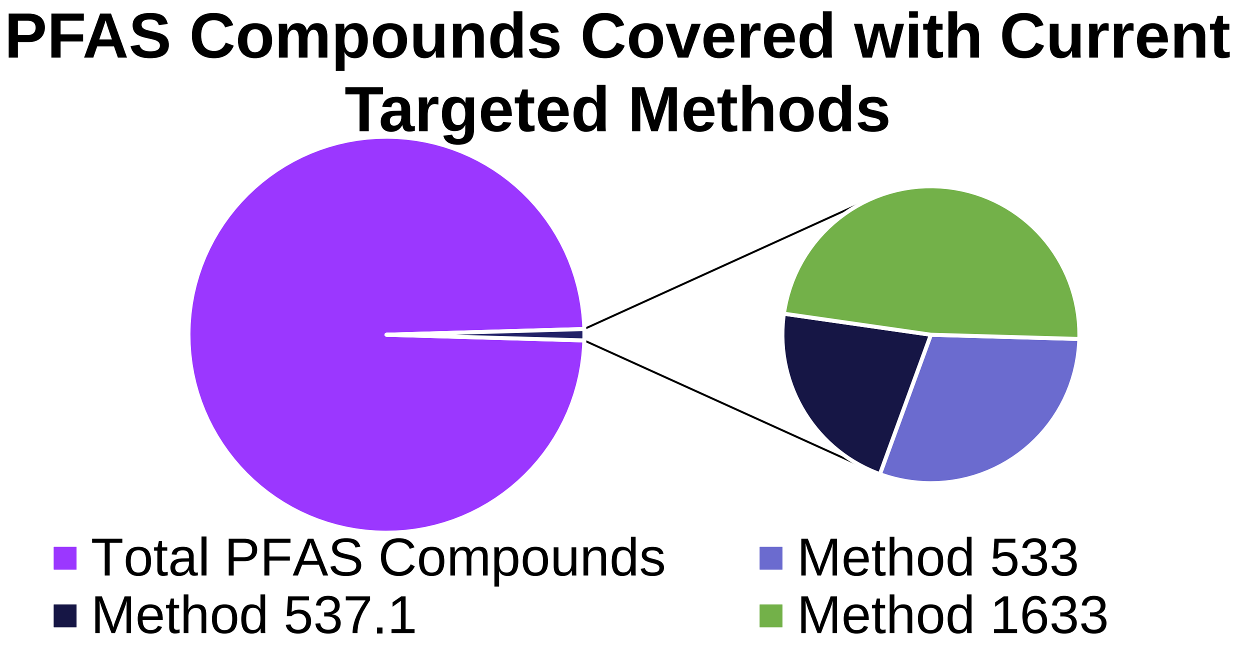
Quantification

Total Fluorine Analysis

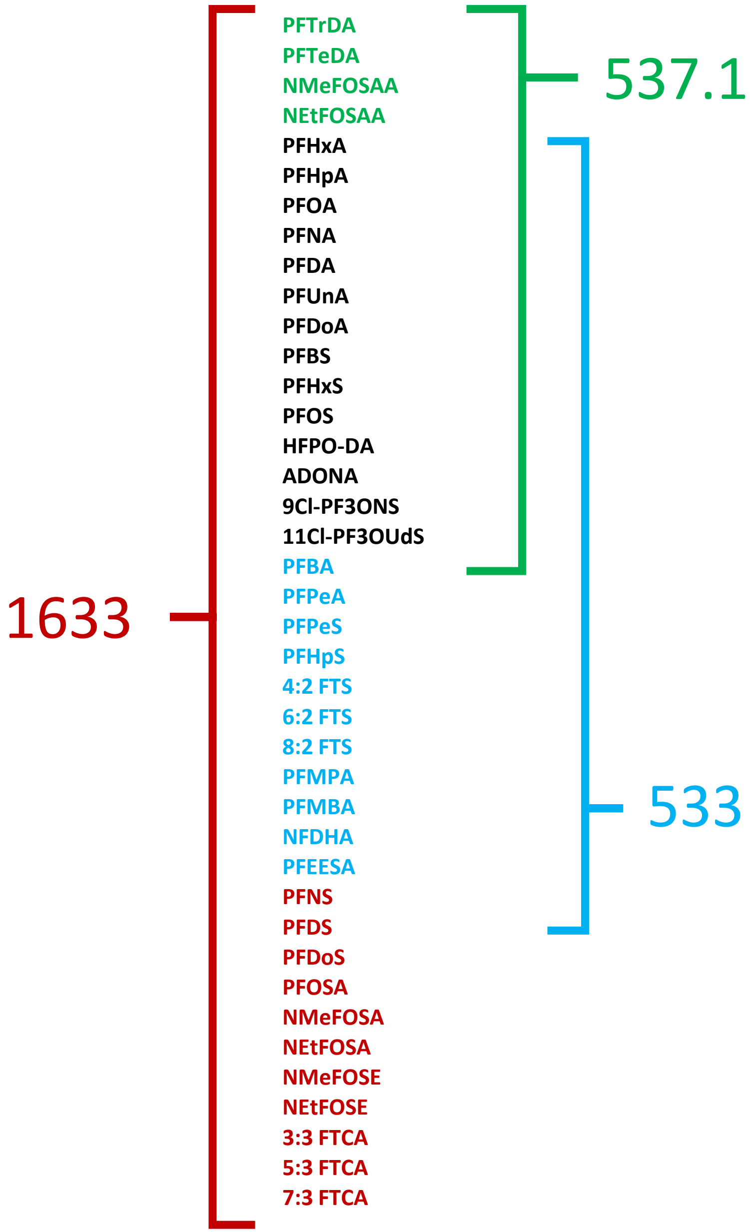
- **Total Organic Fluorine (TOF)**
  - Relatively affordable and quick measurement, minimal data analysis and processing
  - Tool to measure presence of PFAS without analytical standards for every PFAS
  - Screening tool that may help identify relative concentrations of organic fluorine
  - Information may help inform decision making
  - Sample preparation methods balance selectivity and inclusivity



PFAS Analytical Coverage



- PFAS are a group of nearly 15,000 synthetic chemicals, according to the U.S. EPA CompTox database*
- Analytical standards available for ~100 PFAS
- Targeted methods capture <0.3% of individual PFAS chemicals



1633

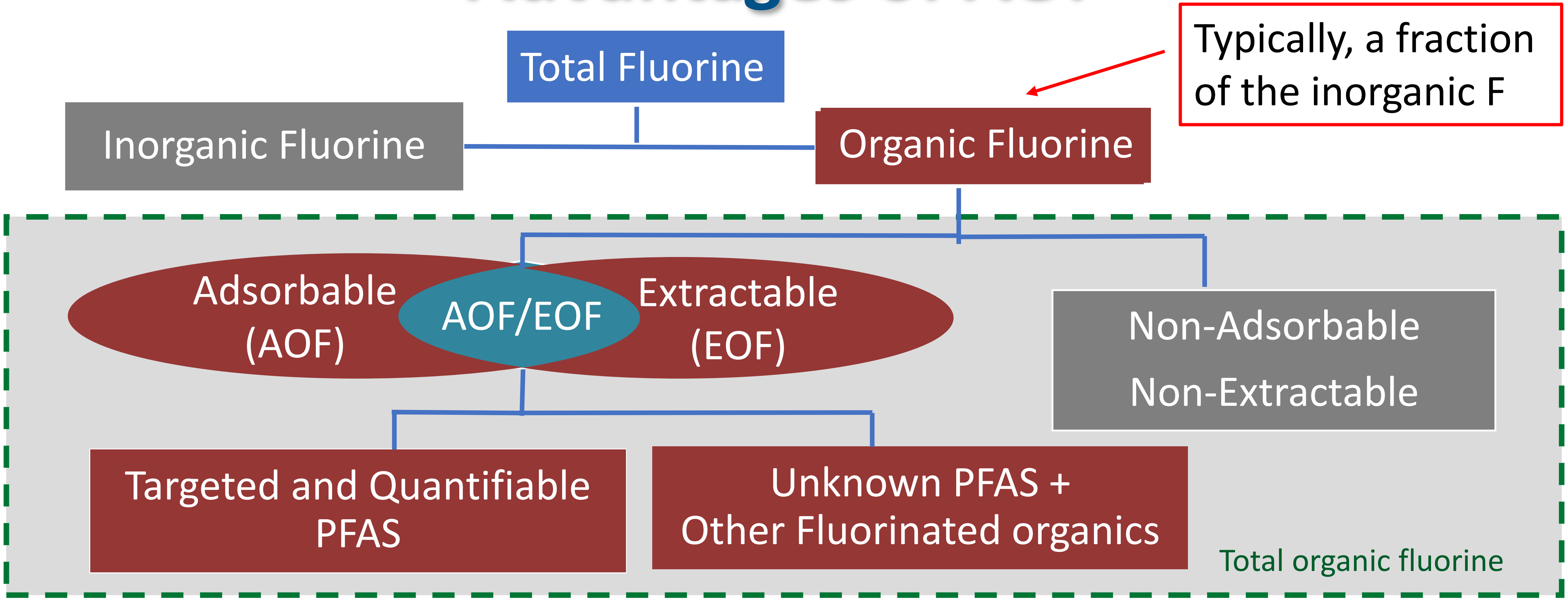
PFTrDA
PFTeDA
NMeFOSAA
NEtFOSAA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnA
PFDoA
PFBS
PFHxS
PFOS
HFPO-DA
ADONA
9Cl-PF3ONS
11Cl-PF3OUdS
PFBA
PFPeA
PFPeS
PFHpS
4:2 FTS
6:2 FTS
8:2 FTS
PFMPA
PFMBA
NFDHA
PFEESA
PFNS
PFDS
PFDoS
PFOSA
NMeFOSA
NEtFOSA
NMeFOSE
NEtFOSE
3:3 FTCA
5:3 FTCA
7:3 FTCA

537.1

533

*https://comptox.epa.gov/dashboard/chemical-lists/PFASSTRUCT

Advantages of AOF



Total Fluorine

Inorganic Fluorine

Organic Fluorine

Typically, a fraction of the inorganic F

Adsorbable (AOF)

AOF/EOF

Extractable (EOF)

Non-Adsorbable

Non-Extractable

Targeted and Quantifiable PFAS

Unknown PFAS + Other Fluorinated organics

Total organic fluorine

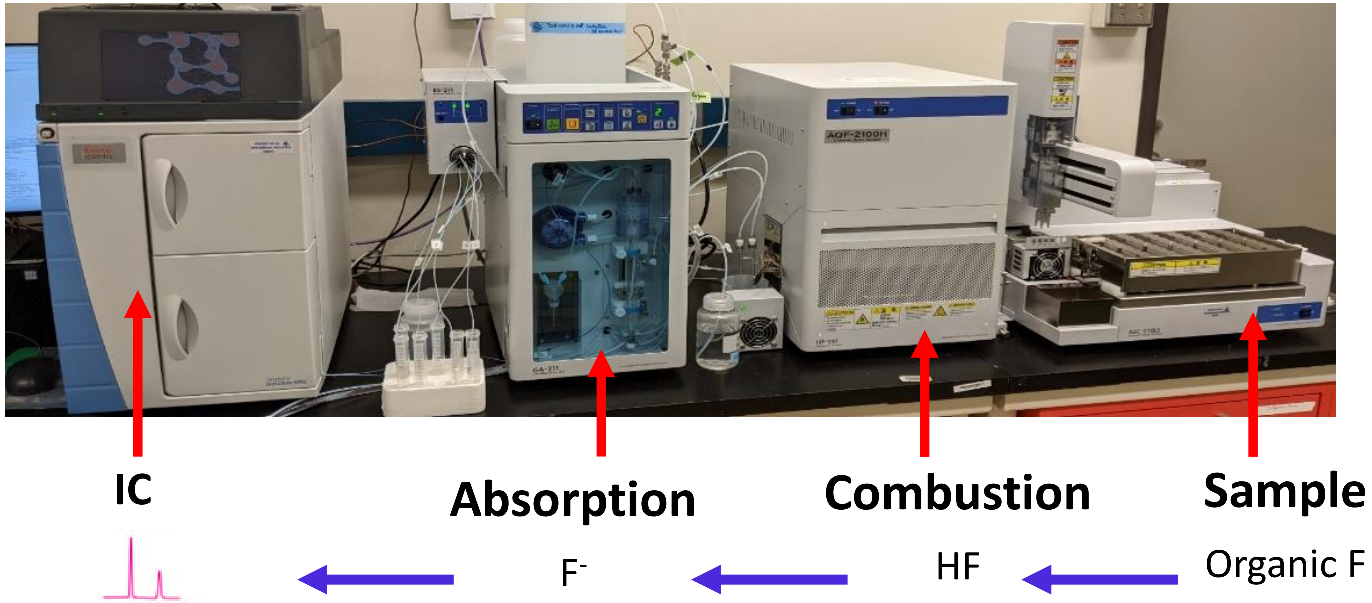
- ☐ Targeted PFAS methods need commercially available standards
- ☐ Best risk assessment will be achieved if as many PFAS are included in the method as possible.
- ☐ Measurements using these techniques will include all adsorbable/extractable organic fluorine.
- ☐ Technique does not distinguish between PFAS, fluorinated pharmaceuticals, agrochemicals

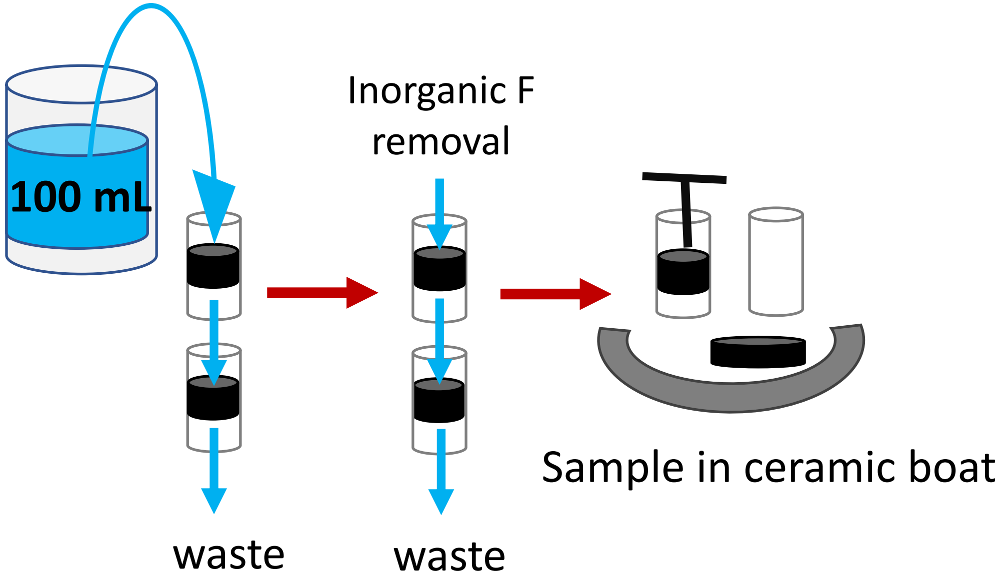
Combustion Ion Chromatography (CIC)

- Technique to measure fluorine by converting fluorine to fluoride
- High temperature furnace breaks C-F bond, released fluorine is captured as fluoride ion
- Adsorbable Organic Fluorine (AOF) – Organic fluorine is adsorbed onto granular activated carbon (GAC)
- Co-adsorbed inorganic fluoride is removed with a nitrate wash
  - ✓Advantages: sample preconcentration; retains many organic compounds
  - ✓Limitations: breakthrough of C_4 and smaller PFAS chains; retains many organic compounds that may interfere in analysis, hydrophobic PFAS adsorb to bottles, extraction units

Total Fluorine Analysis - AOF

- Screening method adsorbs contaminants onto granular activated carbon, removal of inorganic fluoride with nitrate solution, followed by combustion of the carbon

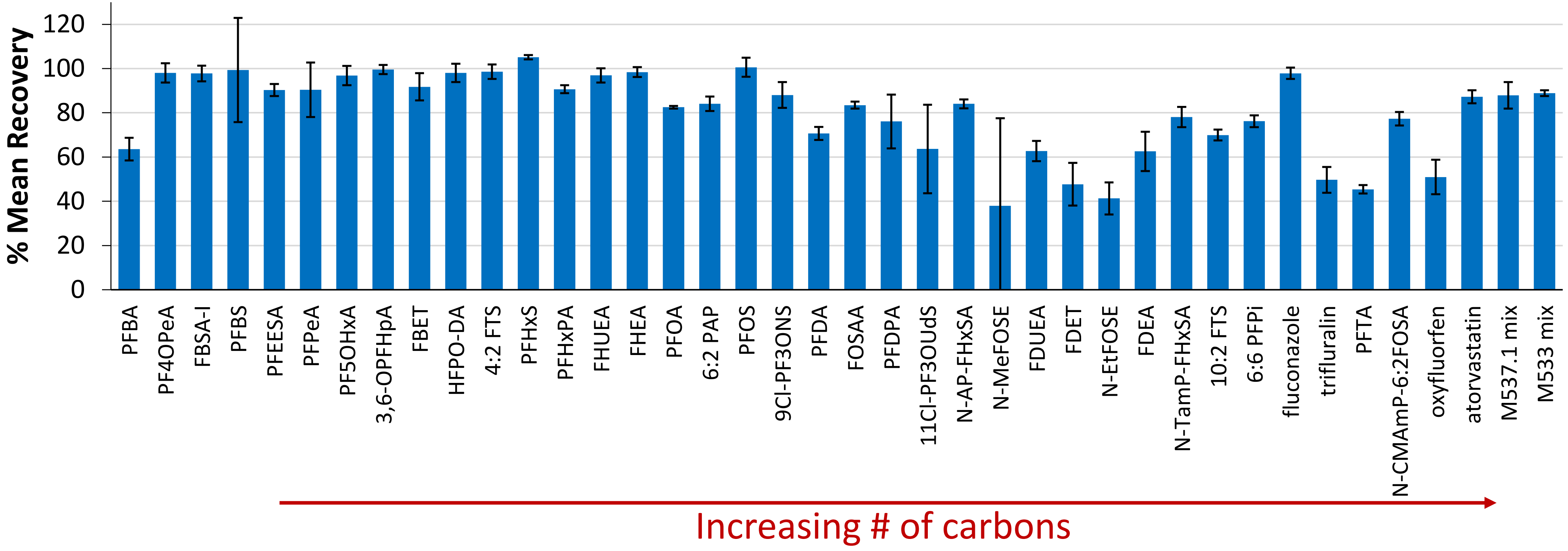




Background fluoride contamination (reagents, materials) will significantly impact detection limit

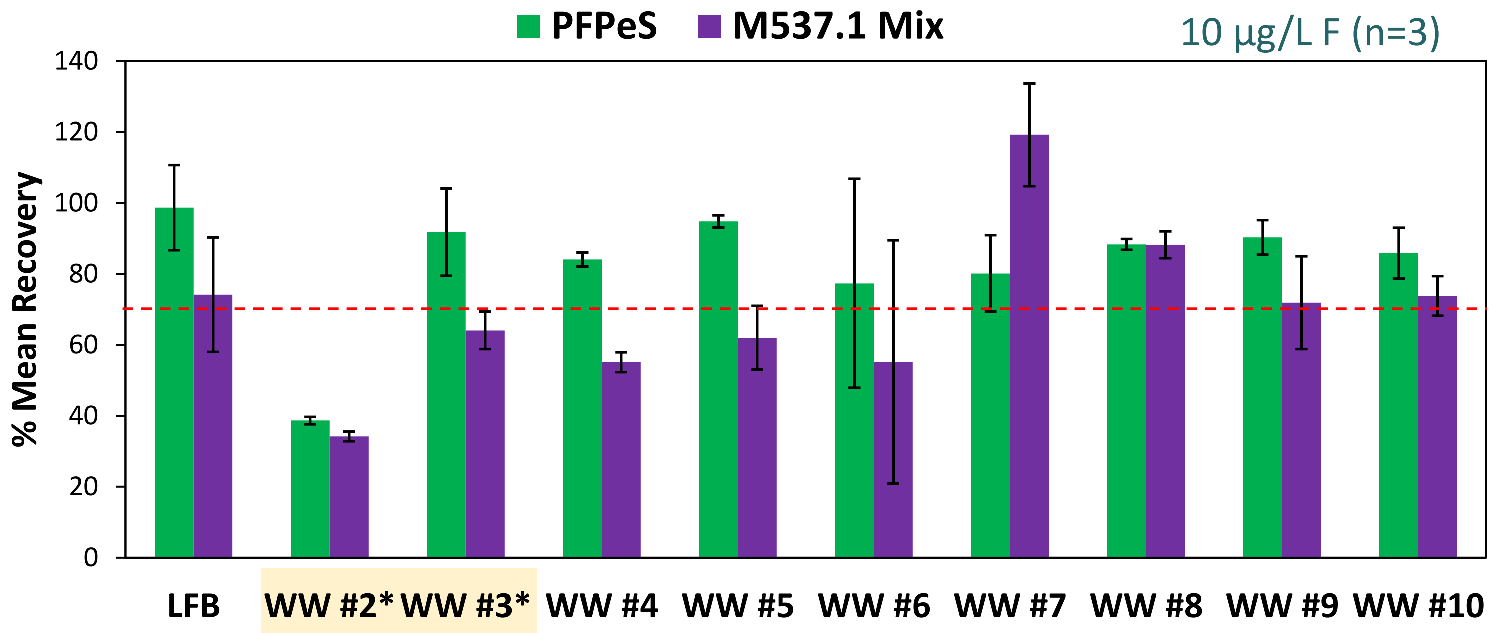
AOF Performance Data

34 PFAS, 2 pesticides, 2 pharmaceuticals, 2 PFAS mixtures in deionized water



- Hydrophilic PFBA (C_4) not well retained on GAC in 100 mL sample volume
- Hydrophobic PFAS tend to adsorb to surfaces thus poor recoveries with high RSDs
- Recovery of mixtures will depend on composition/characteristics of organofluorine
- Technique does not distinguish between PFAS, fluorinated pharmaceuticals, agrochemicals

Recovery in Wastewaters



* 20 µg/L spike due to native AOF >20 µg/L

Wastewater Sample Characterization

Sample #	Source	TSS	TDS	O&G
WW #2*	Landfill leachate	168	4564	0.67
WW #3	Metal finisher	188	3681	1.1
WW #4	POTW Effluent	244	403	11
WW #5	Hospital	5.51	384	0.97
WW #6	POTW Influent	72	772	3.9
WW #7	Bus washing station	29.0	509	23
WW #8	Power Plant	8.97	143	0.33
WW #9	Pulp and paper effluent	37	1992	187
WW #10	POTW Effluent	9.69	893	0.0

- WW #2 & 3 had to be off-line vacuum filtered due to high total dissolved solids (TDS)
- Difficult to get homogeneous replicates with high TSS samples if not filtered (WW #6)
- Largest matrix effects were observed in WW #2 (low recovery) and #7 (high recovery)

Method Detection Limit

PFHxS used as source of organofluorine.

Analyte	Fluoride Fortified Conc. (µg/L)	MDL (µg/L)
AOF	4.9	2.3

- ☐ Consistent with literature for 100 mL samples
- ☐ Significantly higher than HAs or DW regulations
- ☐ MDLs can be lowered if sample size increased
  - ✓ Larger sample sizes will decrease hydrophilic analyte recoveries
  - ✓ Larger samples sizes only possible with waters low in total suspended solids (quartz wool helps)

AOF Method Publication

DOI: 10.1039/D2AY01121B (Paper) *Anal. Methods*, 2022, **14**, 3501-3511

Development of a standardized adsorbable organofluorine screening method for wastewaters with detection by combustion ion chromatography†

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Received 11th July 2022 , Accepted 16th August 2022

1621 Multi-Lab Validation Study

Validation Study:
- 9 labs completed the validation study

Matrix spike results:
- 96% of matrix spikes had recoveries between 50-150%
- PFHxS, PFBA, PFOS, and PFAS mix tested

Blanks and contamination
- Pooled MDL: 1.5 ug/L
- Max MDL: 2.9 ug/L
- No difference between instruments
- High method blanks due to GAC column lots
- Strict cleaning protocols are necessary to minimize background

Final QC Acceptance Criteria
- IPR set at 80-120%
- OPR maintained at 70-130%
- MS/MSD of 50 – 150% and a Relative Percent Difference (RPD) limit of ≤ 30%

Sample	**Industry Type**
Sample #1	POTW-1
Sample #2	Dairy Effluent
Sample #3	Hospital Effluent
Sample #4	Metal Finisher
Sample #5	POTW-2
Sample #6	Bus Washing Station
Sample #7	Pharmaceutical Effluent
Sample #8	Industrial Effluent
Sample #9	POTW-3

https://www.epa.gov/system/files/documents/2024-01/method-1621-mlvs-report-with-appendix-1-30-24.pdf

Adrian Hanley (OW)

Use Under Clean Water Act

Method Defined Parameter – 40 CFR Part 136

- Parameter defined solely by the method used to determine the analyte
- Estimates aggregate concentration of organofluorine compounds that are retained on method specified sorbent

NOTE: Method 1621 is not nationally required for CWA compliance until the EPA has promulgated it through rulemaking

Questions regarding CWA and Method Update Rule for 1621/1633:

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Conclusions

- **Office of Water has published a final version of Method 1621**
  - https://www.epa.gov/system/files/documents/2024-01/method-1621-for-web-posting.pdf
    Note: Method could undergo revision during the rulemaking process

- **Broadly screen for thousands of PFAS at low single digit ppb levels that targeted methods miss**
  - Does not quantify all PFAS with the same accuracy
  - Does not identify which PFAS are present
  - Does not give specific PFAS concentration, results reported as $\mu g/L\ F^-$
  - Does not distinguish between PFAS and other fluorinated chemicals

Contact

Acknowledgements

OW EPA methods 1621 and 1633 –Adrian Hanley, S. Bekah Burket

Questions?
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