



SAFE AND SUSTAINABLE WATER RESOURCES RESEARCH PROGRAM

EPA Method Development Update: Per- and Polyfluoroalkyl Substances (PFAS)

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Overview

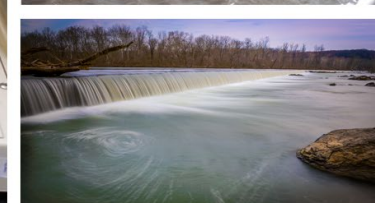
Drinking Water Revision 1 (537.1)

Drinking Water Draft Method 533

SW-846 8328

ASTM D7968

Emerging techniques to determine
“Total” PFAS





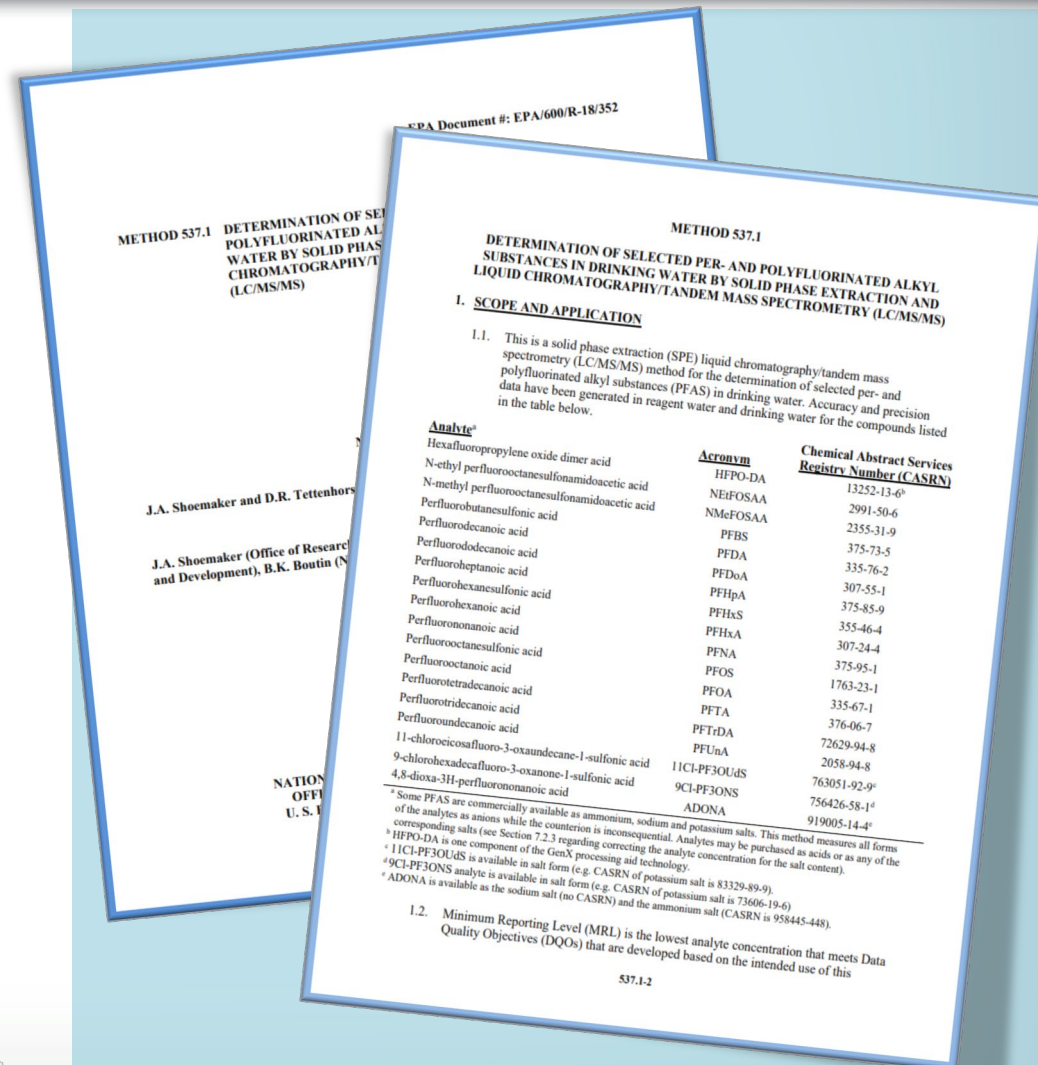
Drinking Water Method 537: Revision I

- **Update: External lab validation for additional analytes by 537**

- Perfluoro-2-propoxypropanoic acid (GenX chemical HFPO-DA, CAS 13252-13-6)
- Potassium 9-chlorohexadecafluoro-3-oxanone-1-sulfonate (9Cl-PF3ONS, CAS 73606-19-6)
- Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS, CAS 83329-89-9)
- Sodium dodecafluoro-3H-4,8-dioxanone (ADONA, CAS 958445-44-8)

- **Incorporated clarifications issued in EPA Technical Advisory** epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf

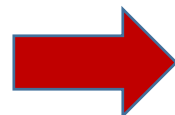
- **Final published method (November, 2018)** epa.gov/water-research/epa-drinking-water-research-methods





Drinking Water Method 537: "Modified"

- Method 537 often modified by analytical laboratories for use on non-drinking water samples.
- If modifications are made that are not explicitly listed in 537 or 537 Revision 1, the method is not considered 537 by EPA.
- The most common modification is inclusion of isotope dilution.



METHOD 537.1

DETERMINATION OF SELECTED PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1. This is a solid phase extraction (SPE) liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of selected per- and polyfluorinated alkyl substances (PFAS) in drinking water. Accuracy and precision data have been generated in reagent water and drinking water for the compounds in the table below.

	Acronym	Chemical Abstract Registry Number (CAS)
Perfluorooctadecanoic acid	HFPO-DA	13252-13-6 ^a
Perfluorooctanesulfonamidoacetic acid	NeFOSAA	2991-50-6
Perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorodecanoic acid	PFBS	375-73-5
Perfluorododecanoic acid	PFDA	335-76-2
Perfluorotetradecanoic acid	PFDoA	307-55-1
Perfluorohexanesulfonic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	355-46-4
Perfluorononanoic acid	PFNA	307-24-4
Perfluorooctanesulfonic acid	PFOS	375-95-1
Perfluorooctanoic acid	PFNA	1763-23-1
Perfluorotetradecanoic acid	PFNA	335-67-1
Perfluorotridecanoic acid	PFNA	376-06-7
Perfluoroundecanoic acid	PFNA	72629-94-1
11-chloroicosafuoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OAS	2058-91-1
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	6305-91-1
4,8-dioxa-3H-perfluorononanoic acid	ADONA	

^a Some PFAS are commercially available as ammonium, sodium and potassium salts. This method is applicable to the corresponding salts (see Section 7.2.3 regarding correcting the analyte concentrations for the counterion).

^b 11Cl-PF3OAS is one component of the GenX processing aid technology.

^c 9Cl-PF3ONS analyte is available in salt form (e.g. CASRN of potassium salt is 6305-91-1).

^d ADONA is available as the sodium salt (no CASRN) and the ammonium salt (CASRN 958445-448).

1.2. Minimum Reporting Level



New Drinking Water Method 533: Under Development

Solid phase extraction/internal standard method targeting PFAS <C12

- Method 537 generally performs poorly for C4 compounds (e.g. PFBA, PFBS).
- Method contains options for using isotope dilution or external standard calibration (or, possibly, two separate methods will be posted).
- EPA Office of Water targeting June 2019 for draft method for public comment.





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8327—Direct Injection*

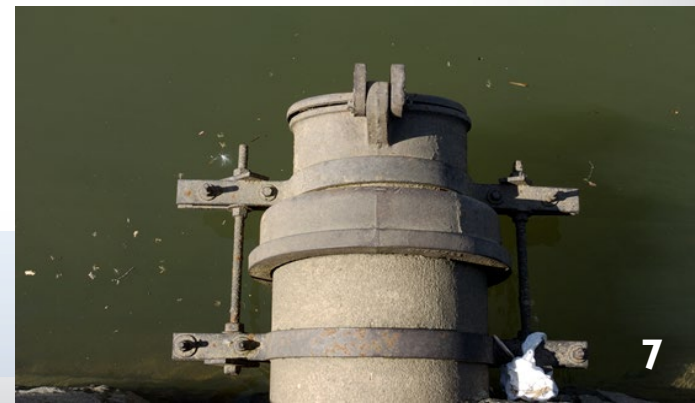
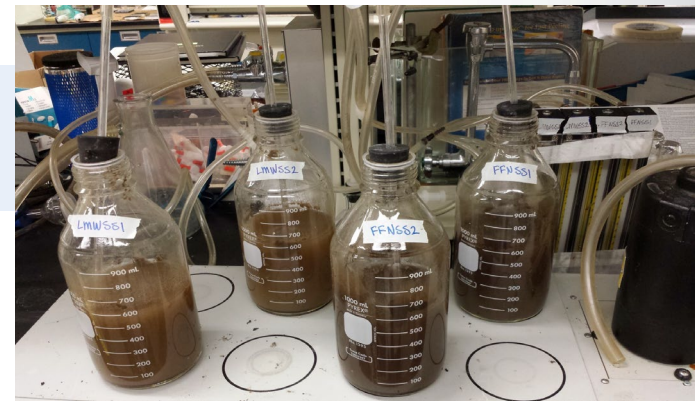
Non-drinking water aqueous matrices:

- Groundwater
- Surface water
- Wastewater

Focuses on...

- Simplicity
- Robustness
- Maximizing throughput for production lab use
- Minimizing sample transfers, extractions, filter steps, chemical additions (e.g., pH adjustments)

Find a balance among sensitivity, ease of implementation, and monitoring requirements.





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8327—Direct Injection*

24 PFAS (including all target analytes in EPA Method 537)

- Commercially available standards (“neat” and isotopically labeled)

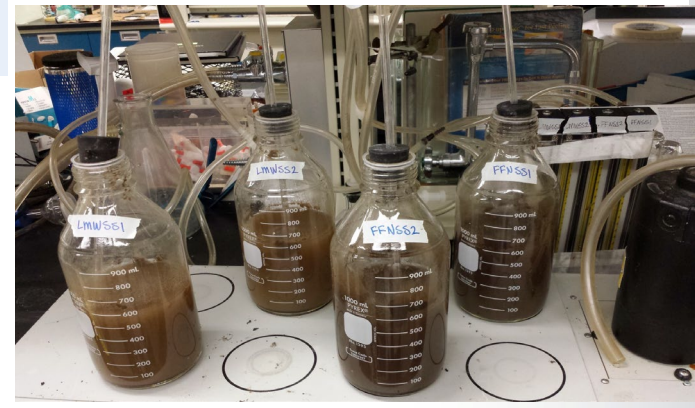
Direct injection based on EPA Region 5/Chicago Lab Method

- Similar to draft American Society for Testing and Materials (ASTM) Method D7979
- Multi-laboratory validation study completed in 2018
- Currently reviewing full data packages and conducting statistical analysis
- Currently Revising final draft

Post draft in early May 2019

(Depending on Office of Management and Budget review requirements)

Target Quantitation Limits: 10 nanogram/L





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8328—Isotope Dilution*

More complex method relative to direct injection, however will

- Likely be more robust for complex matrices (e.g., wastewater influents, biosolids). Account for matrix effects (e.g., sorption) through isotopically marked standard recoveries;
- Afford options to meet DoD requirements; and
- Allow users to perform a deeper dive based on screening (e.g. 8327) results.

Same 24 PFAS analytes plus GenX chemical (HFPO-DA)

Non-drinking water sources

- Surface water
- Groundwater
- Wastewater
- Solids (soils, sediments, biosolids)





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8328—Isotope Dilution*

Based on existing SOP that meets DoD Quality Systems Manual 5.1 Table B-15 requirements

- Many DoD requirements are optional for users that wish to use isotope dilution at non-DoD affiliated sites.

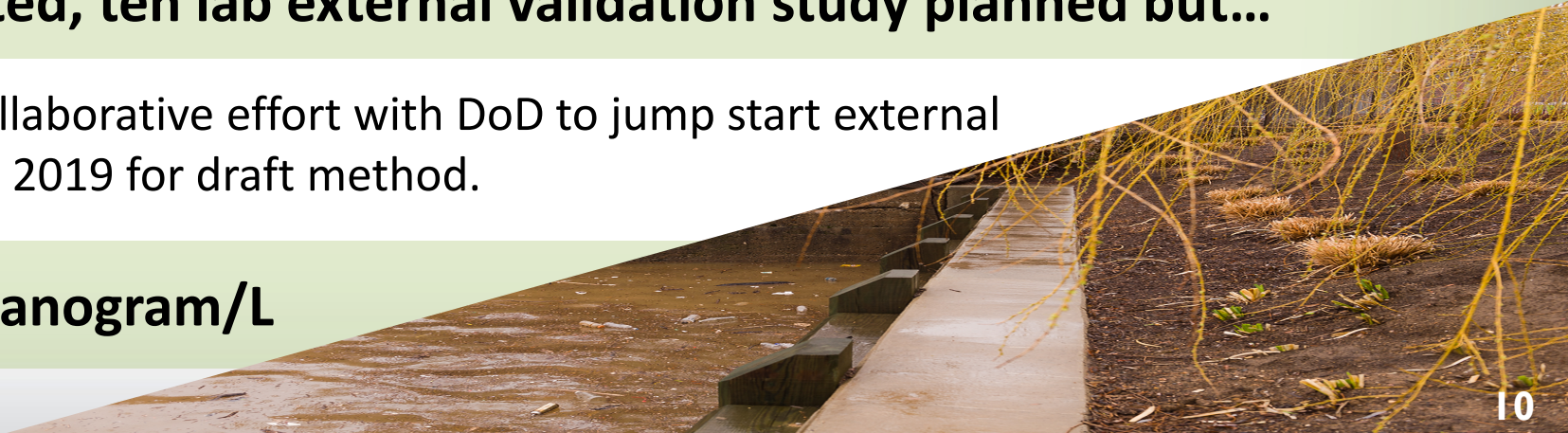
Build in flexibility

- Columns
- Elution schemes

Two lab internal validation started, ten lab external validation study planned but...

- Process is too slow. Exploring collaborative effort with DoD to jump start external laboratory validation. Target Fall 2019 for draft method.

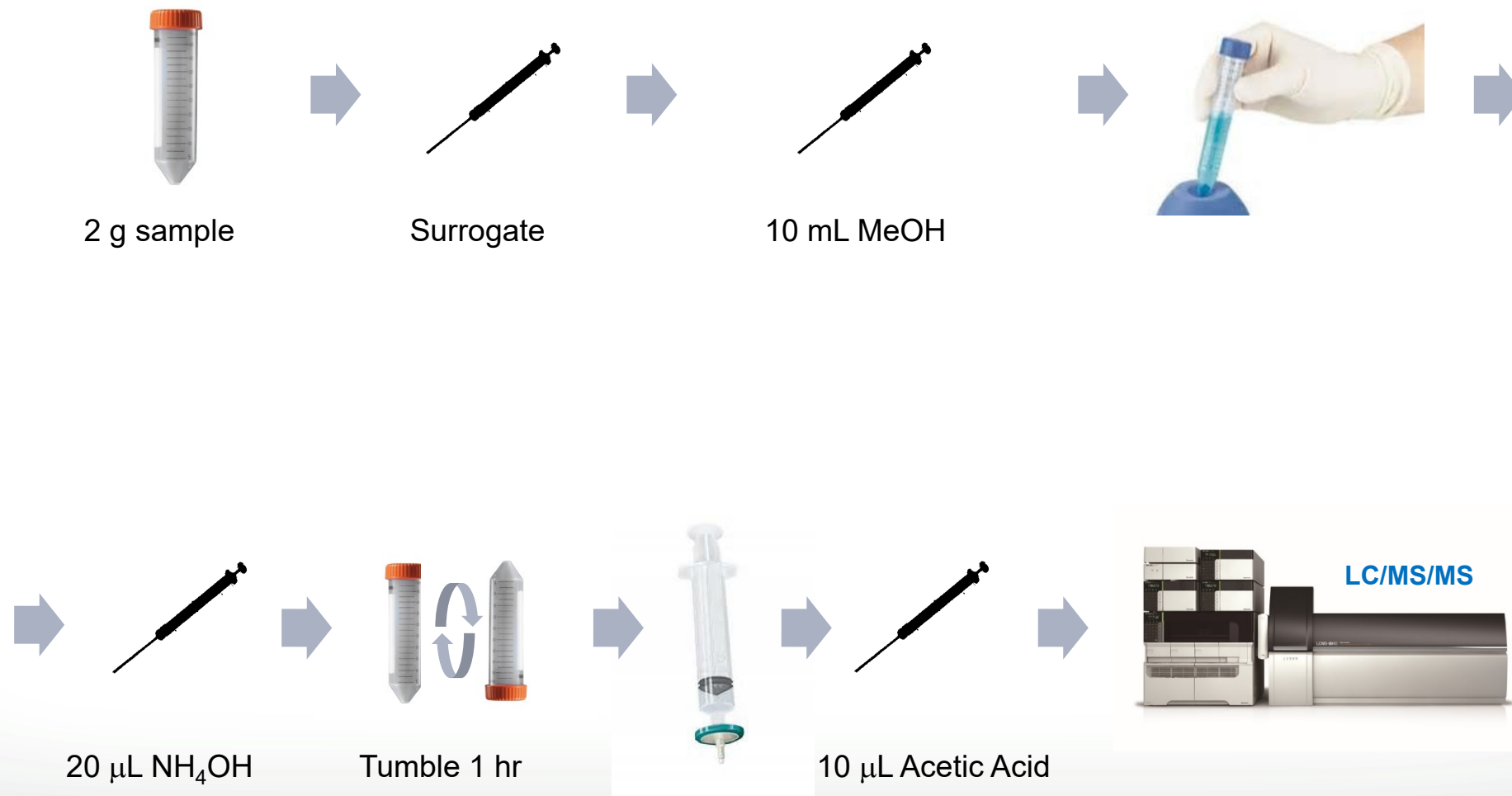
Target Quantitation Limits: 10 nanogram/L



- Environmental solids: soil, sediment, sludge, etc
- Solvent extraction, analysis by LC/MS/MS
- 30 target analytes
- 9 surrogate standards (isotopic-labeled target analytes): Used to monitor analytical method, not used to “correct” the data
- Quantitation with 2 SRMs and ion ratios



ASTM D7968 protocol

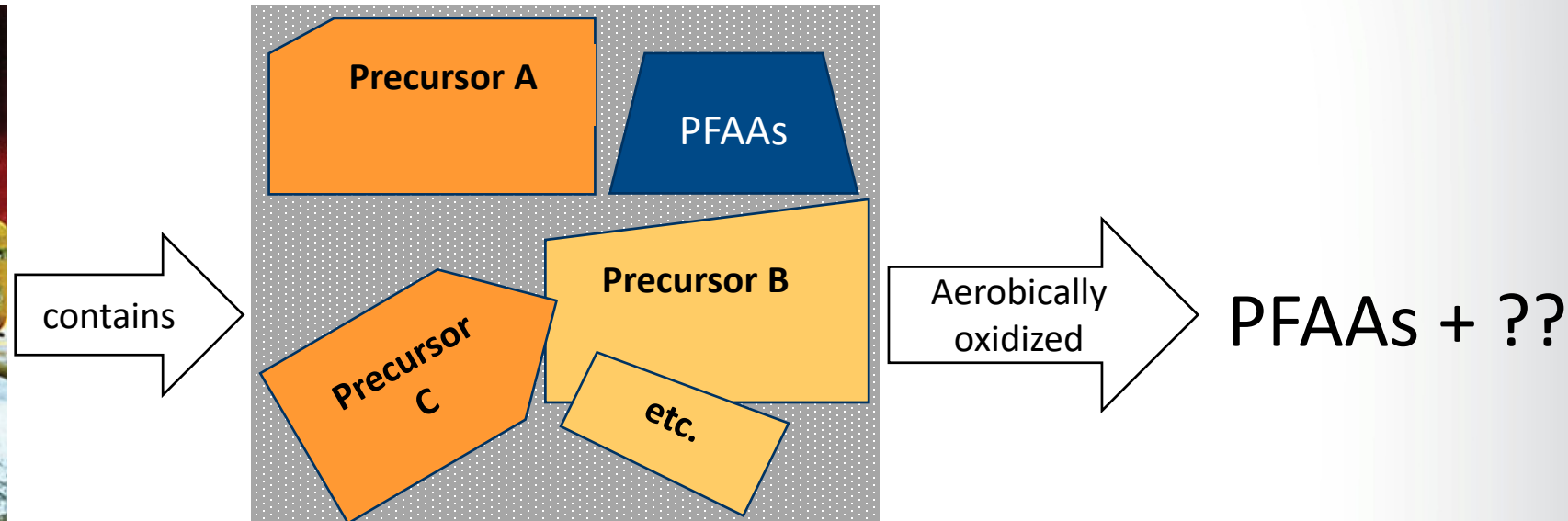


- **Total oxidizable Precursor Assay (TOP Assay)**
- **Total Organofluorine analysis using combustion ion chromatography (TOF)**
- **Non-targeted analysis**



Precursors

PFAS Product (e.g. AFFF)



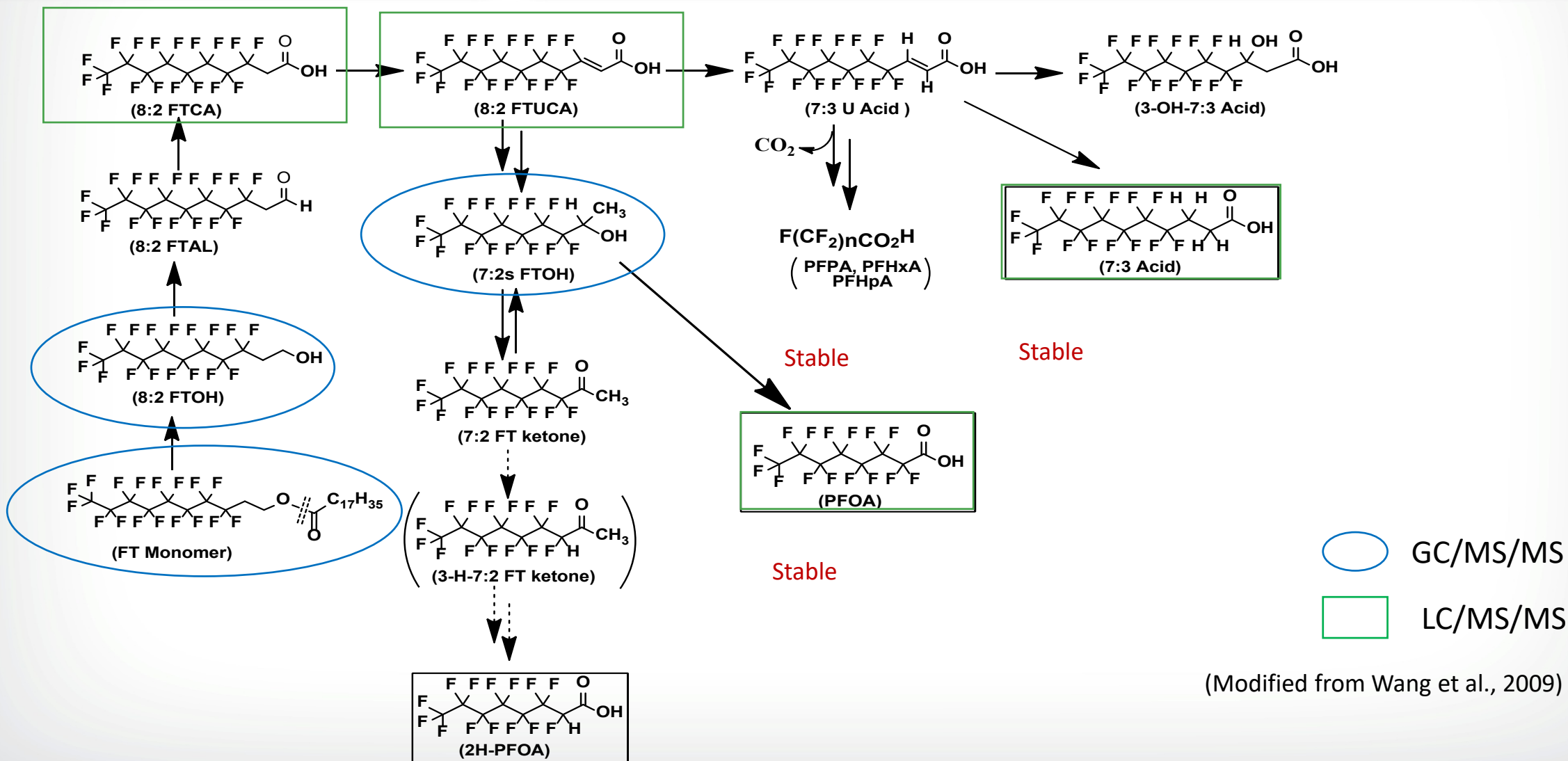
PFAS = Per- & Polyfluoroalkyl Substances includes PFOA or PFOS and precursors

PFAAs = Perfluorinated alkyl acids, includes PFOA and PFOS

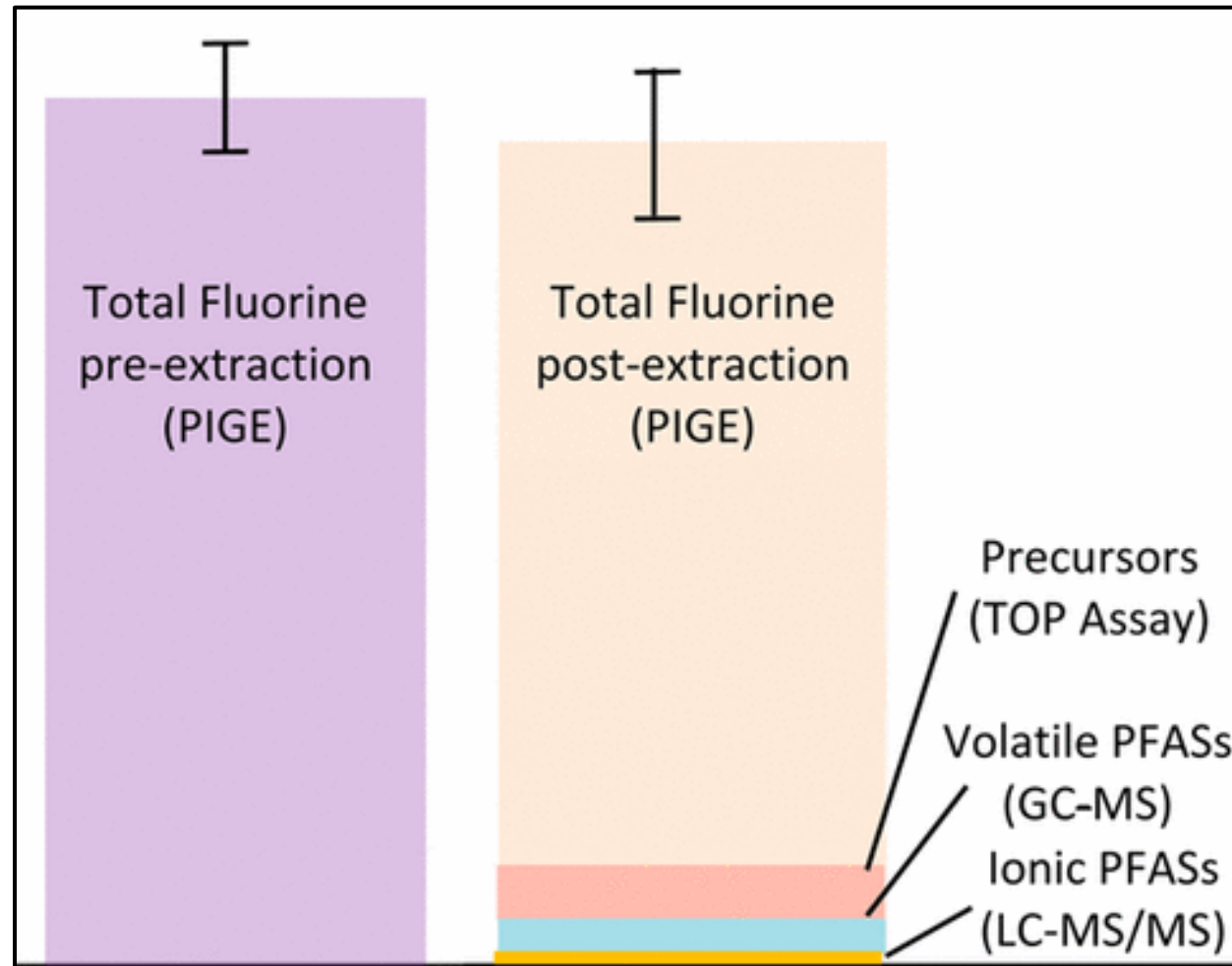
- ◆ PFAAs are more commonly measured
- ◆ Precursors mass may be substantial component of the total product mass
- ◆ Precursors may be degraded to PFAAs over time naturally or during transformations by oxidative treatment systems targeting other contaminants



Transformation to form PFOA



For example... a mass balance for PFAS



Mass balance of based on total fluorine in textiles and papers.

Robel et al, 2017



Targeted Analysis of Precursors

EPA ORD SOPs for Environmental Waters (not DW) and solids

- Water - SPE, analysis by GC/MS/MS
- Solids – solvent extraction, analysis by GCMS/MS

Analytes:

- Fluorotelomer Alcohols(FTOHs)- 4:2, 6: 2, 8:2, 7:2s, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, and 11:1
- Fluorotelomer monomers- 6:2 Fluorotelomer Acrylate (6:2 FTAc), 6:2 Fluorotelomer Methacrylate (6:2 FTMAc), 8:2 FTAc, 8:2 FTMac, 10:2 FTAc, and 10:2 FTMac
- Perfluoro-1-octanesulfonamido-ethanol (FOSE)- 2-N-ethylFOSE (N-EtFOSE), and 2-N-MethylFOSE (N-MeFOSE)

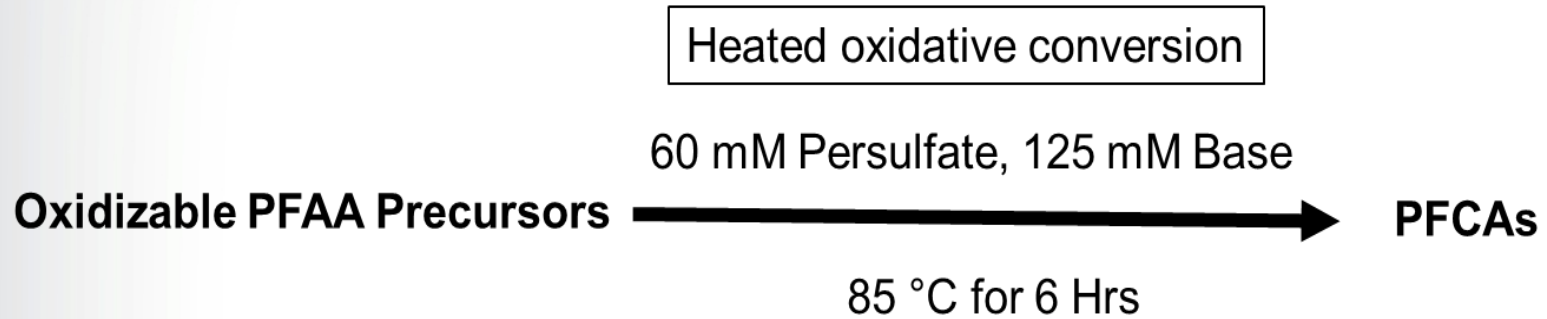
Surrogate standards

- 8:2 MFTOH
- d7-MeFOSE

Quantitation similar to ASTM method – monitoring 2 SRMs and evaluating ion ratios



Total Oxidizable Precursor Assay (TOP Assay)



$$\text{Total Oxidizable Precursors} = \text{PFCAs}_{\text{after oxidation}} - \text{PFCAs}_{\text{before oxidation}}$$

- Applicable for both aqueous and solid matrices
- Conservative estimate of the total concentration of PFAA precursors

- Does not identify individual precursor compounds
- More expensive technique - Sample needs to be analyzed 2 times for PFAAs – before and after oxidation
- Available in commercial labs and under evaluation at EPA, however, no standard methods currently exist.



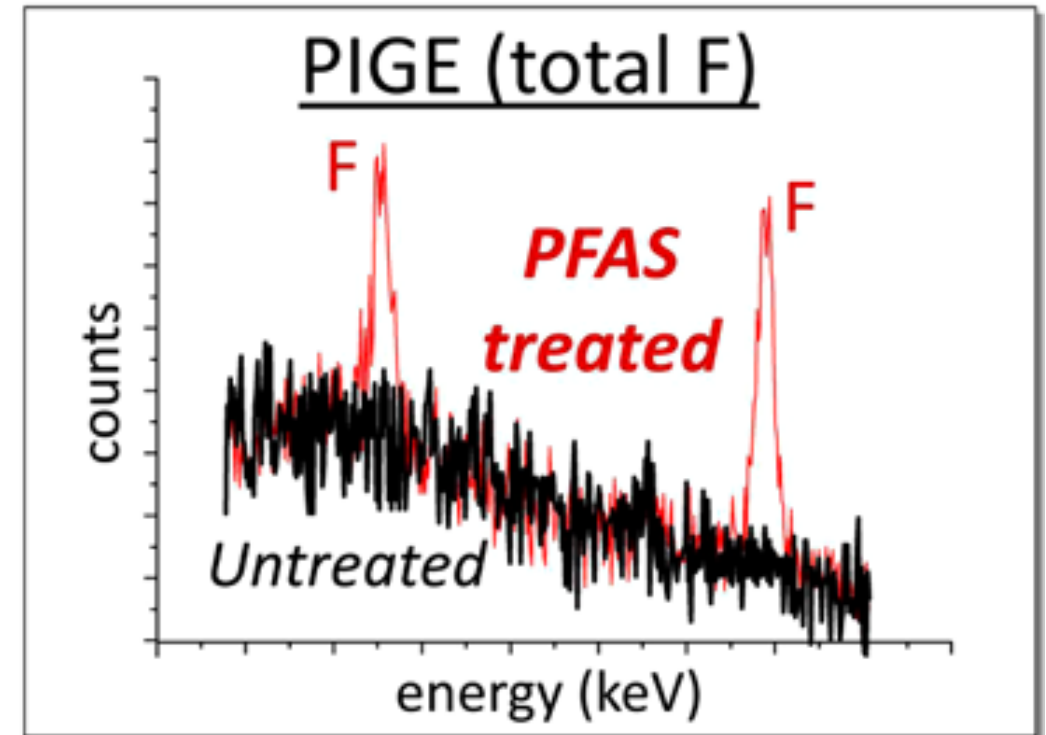
Total Organofluorine Analysis using Combustion Ion Chromatography (TOF)



- No specialized or costly instrumentation required
- Applied for aqueous matrices and blood samples
- Removing the background inorganic F^- from the sample is important to make sure that the reported F^- is organic
- Can be developed on a wide commercial scale

Particle Induced Gamma-Ray Emission (PIGE) Technique

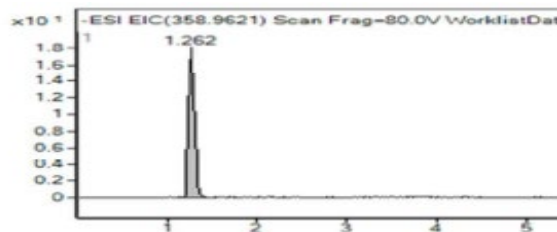
- Surface analysis - measures atomic fluorine
- Potential advantage - easily applied to complex fluoropolymer matrices which are difficult to extract
- Specialized equipment – Not easily accessible
- Currently available only at University of Notre Dame



Ritter et al. 2017; Schaider et al. 2017

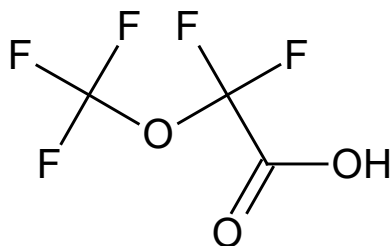
Explore Unknown compounds using High resolution mass spectrometry. Identify a peak in a chromatogram and to ultimately predict the identity of this unknown

↓ Mass spectrometer assigns a high resolution mass for peaks observed in the chromatogram



↓ Software calculates the exact number and type of atoms needed to achieve the measured mass.

↓ Fragmentation experiments allow determination of most likely structure:



Molecular Formula: C₂HF₅O₃
Monoisotopic Mass: 179.984585 Da
[M-H]⁻: 178.977308 Da

↓ Using mass, formula, and structure, identity can be assigned by searching against databases of known compounds

↓ Compare peak to commercial to confirm identification if possible



Grab Sampling



- **Grab sampling is commonly used for PFAS**
- **Consideration needed of personal care products and clothing for potential contamination**
- **Sample bottle should be opened prior to the sampling and dipped inside the water and closed with the lid immediately after sample collection**
- **Pack the sample bottles with individual PFAS free zip-lock bags to separate samples and pack with regular ice**
- **Overnight shipment to analytical laboratory**





Passive Sampling

- **Advantages:**
 - **Low-cost and time-integrative sampling approach proven useful for broad range of contaminants**
 - **Accumulates dissolved contaminants through diffusion**
 - **QC samples include field blanks and laboratory blanks**
- **Issues:**
 - **Commonly used for neutral compounds**
 - **PFAS are ionic - anions**
 - **Challenges for sampling ionized compounds**
- **Types of Passive Samplers**
 - **Polar Organic Chemical Integrative Sampler (POCIS)**
 - **Anions (e.g. PFOA, PFOS)**
 - **Used for water sampling**
 - **Polyethylene samplers**
 - **Neutral species - Precursors**
(e.g. 6:2, 8:2 and 10:2 FTOH, Me/Et-FOSA, Me/Et-FOSE)
 - **Used for both water and air sampling**

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Conclusions

- Significant investments in PFAS-related research is starting to show results.
- Standardized methods and sampling approaches are being developed currently.
- Methods and sampling approaches are needed for adequate characterization of sources and PFAS-impacted media
- Air methods for sampling and analyses are under development and will be needed for selected site investigations and monitoring



Contacts for Questions or Comments

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Analytical Challenge:

Linear and Branched Isomers

- Many of the branched isomers are unknown and standards are not available
- Quantifying only linear isomer leads to underestimation of PFAS concentrations
- Importance of isomer specific data:
 - Different physical and chemical properties (water solubility, sorption, transport behavior and bioaccumulation potentials)
 - Treatment and remediation processes
 - Information about their manufacturing sources
 - Need for the pure and well characterized isomeric standards for the accurate measurements of branched and linear PFASs isomers

