

PFAS: Analytical Considerations and Sampling Techniques

 **ENTHALPY**
ANALYTICAL
a Montrose Environmental Group company

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July 25, 2023



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Business Development Manager / Senior Chemist

B.S., Chemistry – College of William and Mary

More than 18 years' experience in environmental analytical chemistry

Laboratory Locations



Market Overview

Enthalpy's clients come from a diverse range of consultants, from private industry to federal, state, and local governments. With a strong industry reputation, we provide contract analytical services to Fortune 100 Companies in **five continents**. Our services support various industries and project types including:

- Electrical and Gas Utilities
- School Districts
- Ports & Shipyards
- Aerospace Industry
- Petroleum Marketing & Refining
- Transportation Agencies
- Legal Groups
- Petrochemical Industry
- Recycling Facilities
- Treatment Facilities
- Municipalities
- Department of Defense
- Landfills
- Manufacturing Facilities

Testing Overview

Full-service environmental testing network,
specializing in:

- Soil
- Sediment/Dredged Soils
- Hazardous Waste
- Wastewater/Stormwater
- Groundwater
- Drinking Water
- Ultra Low Level Metals
- Microbiology
- Low Level Dioxins/Furans (High-Res MS)
- Landfill / Biogas
- Soil Gas
- Ambient/Indoor Air Quality
- Source Emissions
- Product Testing
- Marine Chemistry
- Eco-Toxicity (Bioassay)
- Legionella

Overview of Topics

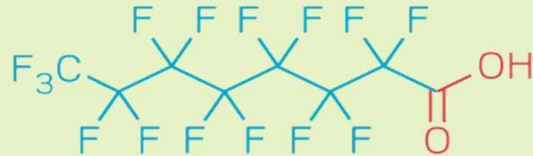
- » Chemical Structures
- » Timelines
- » UCMR 5 Methodology
- » Draft 1633
- » Sampling Techniques



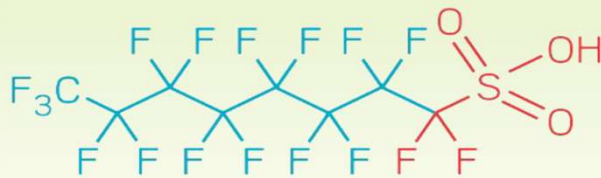
PFAS (Per & Polyfluorinated Alkyl Substances)

Longer Chains & Strong Bonds C8

PERFLUORINATED

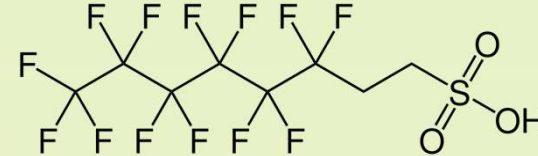


Perfluorooctanoic acid,
PFOA,
CAS 335-67-1



Perfluorooctane
sulfonic acid,
PFOS,
CAS 1763-23-1

POLYFLUORINATED



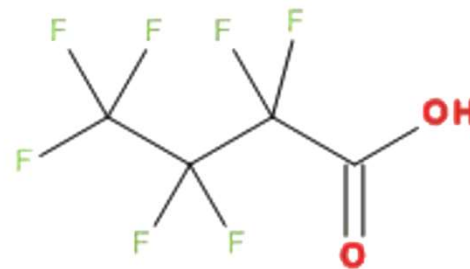
6:2 FTS



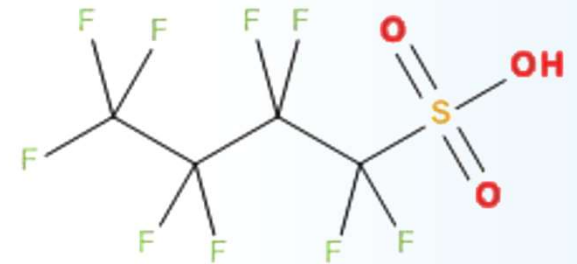
Replacement Compounds

C4 & C6

- » Industry Claims they are safer
- » Precursors are still longer chain C8
- » PFBA-food packaging and film
- » PFBS-surfactants/ repellents, metal plating, pesticides, and flame retardants



PFBA

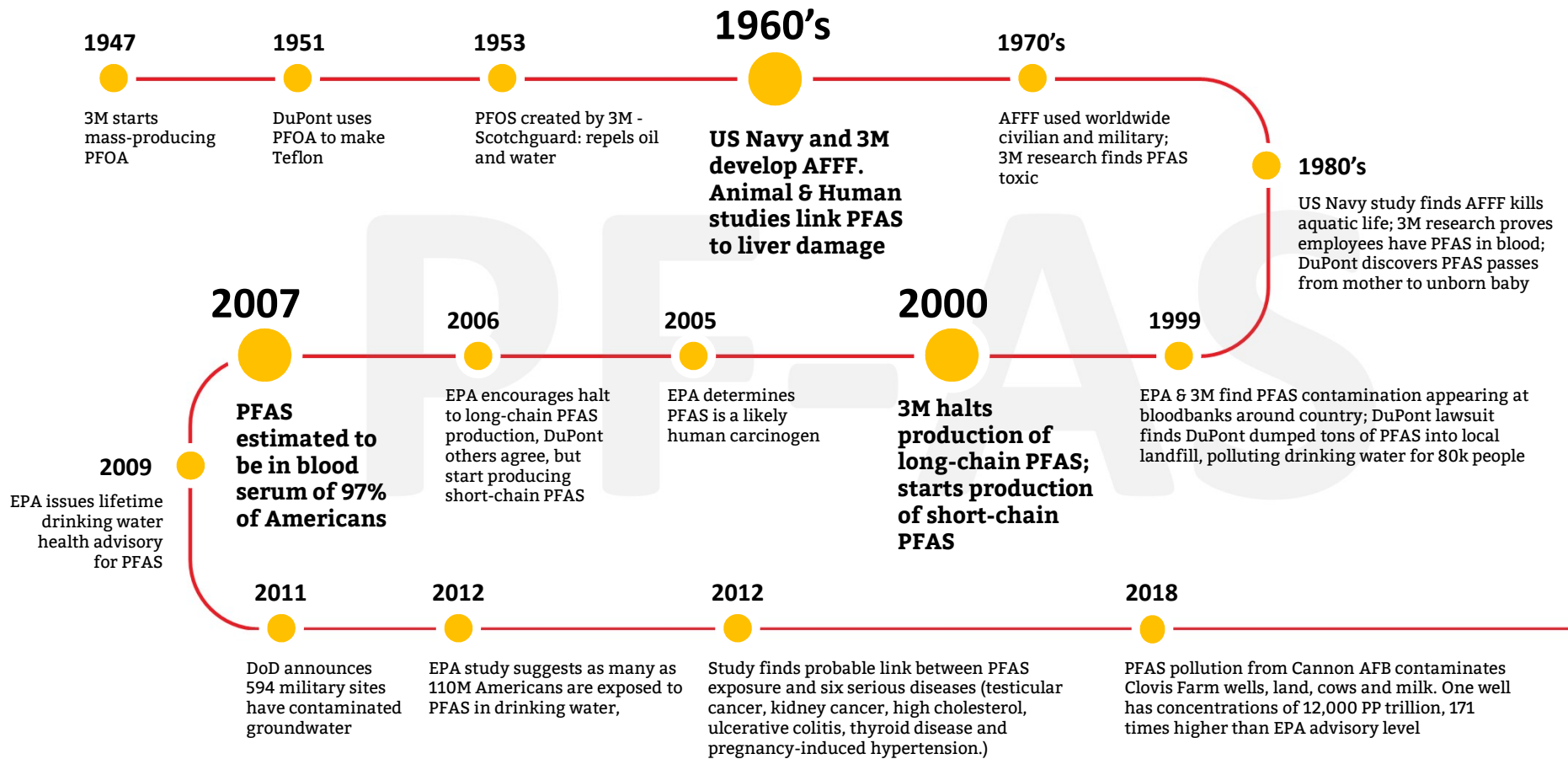


PFBS

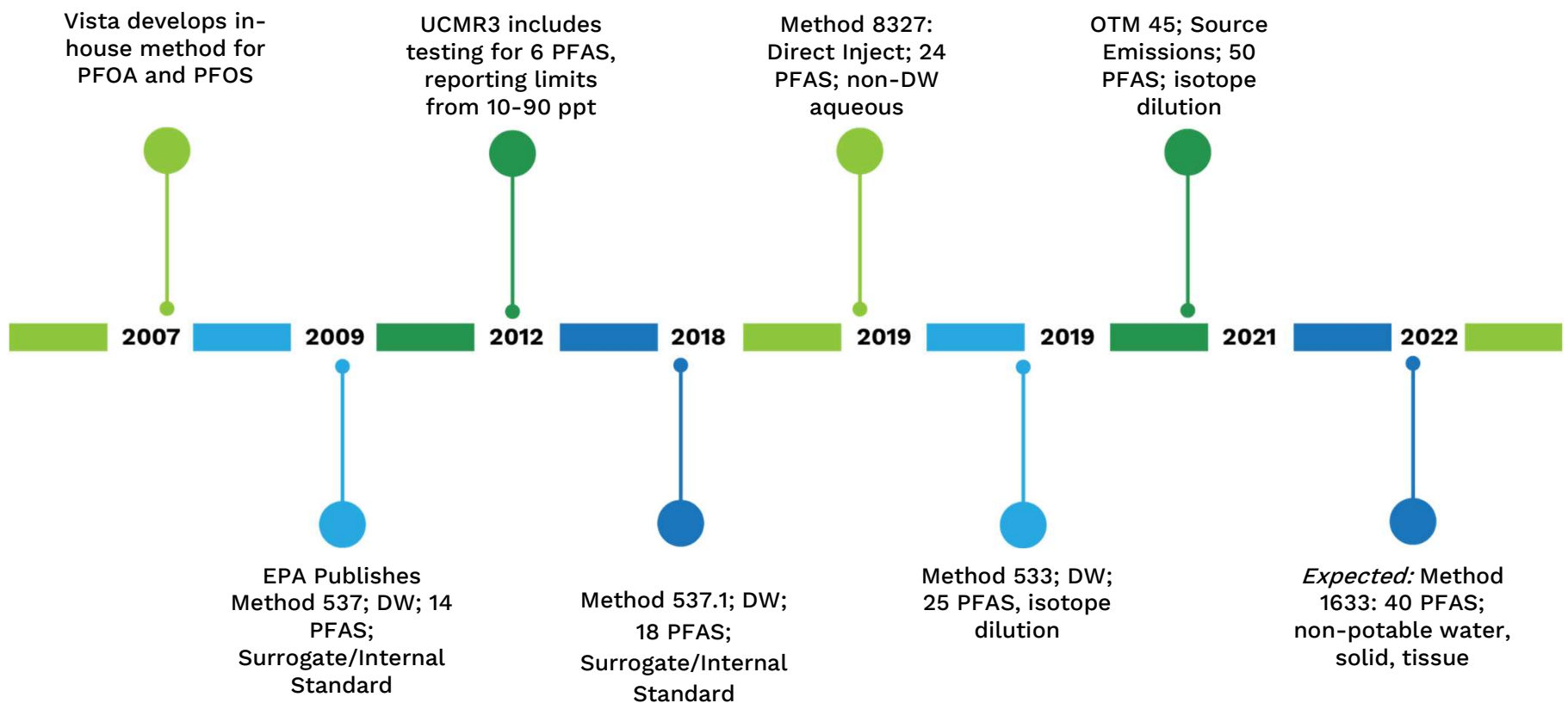


6:2 Fluorotelomer acrylate

The History of PFAS...



Analytical Timeline



The Health Advisory Heard Around the Word

Chemical	2016 HA (ppt)	Current HA (ppt)	Min. RL (ppt)
PFOA	70	0.004	4
PFOS	70	0.02	4
Gen X	NA	10	5
PFBS	NA	2000	3

So does a non detect even mean non detect at such low levels?

The agency uses [health advisories](#) for unregulated contaminants that can cause human health effects and are known (or anticipated) to be present in drinking water. They are **non-enforceable federal limits** but serve as technical guidance for federal, state, and local officials to inform if action is needed to protect public health. These actions can include water quality monitoring, optimizing existing PFAS reduction technologies, and developing strategies to reduce exposure to PFAS

March 2023 – EPA proposes MCLs & Hazard Index

Chemical	MCL
PFOA	4.0 ng/L (ppt)
PFOS	4.0 ng/L (ppt)
PFNA	1.0 (unitless) Hazard Index
PFHxS	
PFBS	
HFPO-DA (commonly referred to as “GenX Chemicals”)	

The MCLs for PFOA and PFOS are “set at the lowest feasible quantitation level”. In an effort to capture the additive effects of PFNA, PFHxS, PFBS and the GenX chemicals, the MCLs incorporate a Hazard Index approach.

According to the agency’s news release, “If finalized, the proposed regulation will require public water systems to monitor for these chemicals. It will also require systems to notify the public and reduce PFAS contamination if levels exceed the proposed regulatory standards.”

March 2023 – EPA Proposes PFAS Regulation in CERCLA

Following the 2021 EPA PFAS Roadmap, in March 2023 EPA released an Advanced Notice of Proposed Rulemaking regarding regulation of PFOA, PFOS and 7 other PFAS compounds via CERCLA:

PFAS Compound – Proposed CERCLA	
PFOA	PFOS
PFBS	PFHxS
PFNA	HFPO-DA
PFBA	PFHxA
PFDA	

March 2023 – NCDEQ Landfill Requirement

On March 14, 2023 NCDEQ Division of Waste Management released a memo to all landfill owners and operators regarding sanitary solid waste facilities, stating that:

- **As of July 1, 2023 all Groundwater, Surface Water, Leachate samples must be tested for PFAS**
- Analysis required by **Draft EPA 1633**
- Must use a lab with appropriate accreditation (DoD-ELAP)
- All data must be reported to the state
- No mention of how this data will be used, i.e., to determine future monitoring plans, etc.

Many landfills have already set their budgets (FY July-July) and anticipate a tremendous burden of cost with sampling.

NC is the first – they certainly won't be the last.



**UCMR 5: What are its
impacts in regards
to PFAS?**



Unregulated Contaminant Monitoring Rule: **UCMR 5**

- » UCMR was established to **monitor unregulated contaminants** in drinking water every 5 years
- » All large systems **serving over 10,000 people** are required to monitor
- » **EPA pays for small systems** testing 3,300 to 10,000
- » A **representative sample** is taken from systems serving less than 3,300 people
- » **UCMR 5** was published in the Federal Registry March 11, 2021
- » **EPA does it's own certification of labs**
- » **29 PFAS** and Lithium
- » **Sampling term:** January 2023–December 2025
- » EPA expects to post **preliminary data mid 2023** and update the date quarterly moving forward
- » **UCMR 3** occurred January 2013 –December 2015 and reported
- » **UCMR 3 reported** 6 PFAS–PFOS, PFOA, PFNA, PFHxS, PFHpA, and PFBS

ANALYTE	537.1	533
PFEESA		•
HFPOA-DA/Gen X	•	•
NFDHA		•
PFOS	•	•
PFUdA	•	•
N-MeFOSAA	•	
PFPeA		•
PFPeS		•
6:2 FTS		•
N-EtFOSAA	•	
PFHxA	•	•
PFDoA	•	•
PFOA	•	•
PFDA	•	•
PFHxS	•	•
PFBA		•
PFBS	•	•
PFHpA	•	•
PFHpS		•
PFNA	•	•
PFTeDA	•	
PFMOPrA		•
8:2 FTS		•
PFTrDA	•	
9Cl-PF3PONS	•	•
4:2 FTS		•
11Cl-PF3OUdS	•	•
PFMOBA		•
ADONA	•	•

UCMR 5 PFAS Methodology

EPA 537.1

- » EPA 537/537.1-Drinking Water, Required for demonstrating compliance, 18 compounds, not all states accredit states accredit
- » Field Blank and MS/MSD
- » 14 day hold time
- » Does not use isotope dilution
- » Does not do a great job on the shorter chain PFAS compounds like PFBS

ANALYTE
HFPOA-DA/Gen X
PFOS
PFUdA
N-MeFOSAA
N-EtFOSAA
PFHxA
PFDoA
PFOA
PFDA
PFHxS
PFBS
PFHpA
PFNA
PFTeDA
PFTTrDA
9Cl-PF3PONS
11Cl-PF3OUdS
ADONA

UCMR 5 Methodology

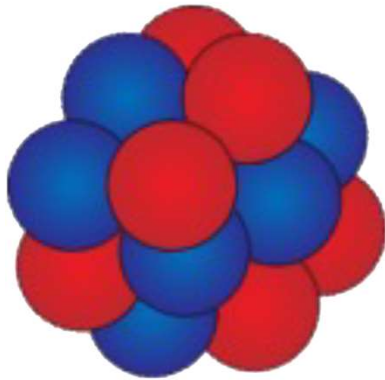
EPA 533

- » EPA 533-Drinking Water, Isotope Dilution, 25 compounds
- » **Uses isotope dilution!!!**
- » Field Blanks and MS/MSD
- » **28 day hold time**
- » Can cause the lab a lot of rework due to extra QC parameters. This rework can cause late date or even worse samples to go out of hold time.
- » 25 PFAS reported

ANALYTE	ANALYTE
PFEESA	PFBA
HFPOA-DA/Gen X	PFBS
NFDHA	PFHpA
PFOS	PFHpS
PFUdA	PFNA
PFPeA	PFMOPrA
PFPeS	8:2 FTS
6:2 FTS	9Cl-PF3PONS
PFHxA	4:2 FTS
PFDoA	11Cl-PF3OUdS
PFOA	PFMOB
PFDA	ADONA
PFHxS	

Let's Talk....Isotopes

1 Dalton (Da) = $1.66053906660(50) \times 10^{-27}$ kg



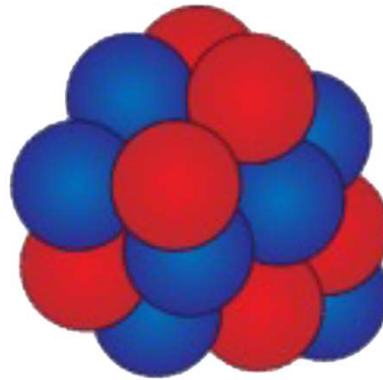
Carbon-12

98.9%

6 protons

6 neutrons

Atomic weight:
12 Da exactly



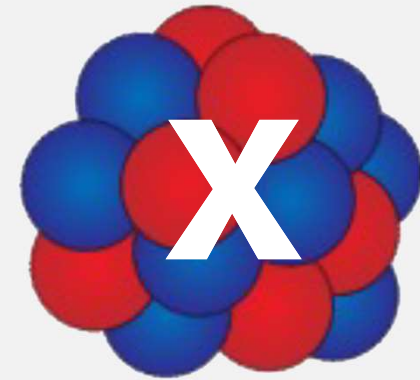
Carbon-13

1.1%

6 protons

7 neutrons

Atomic weight:
13.00335483521(23) Da



UNSTABLE

Carbon-14

<0.1%

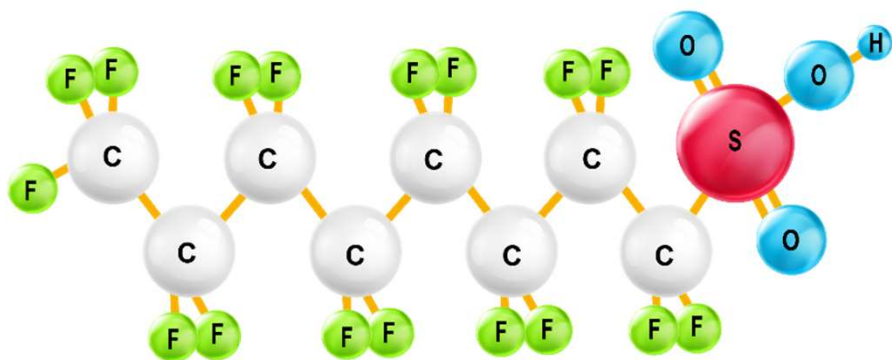
6 protons

8 neutrons

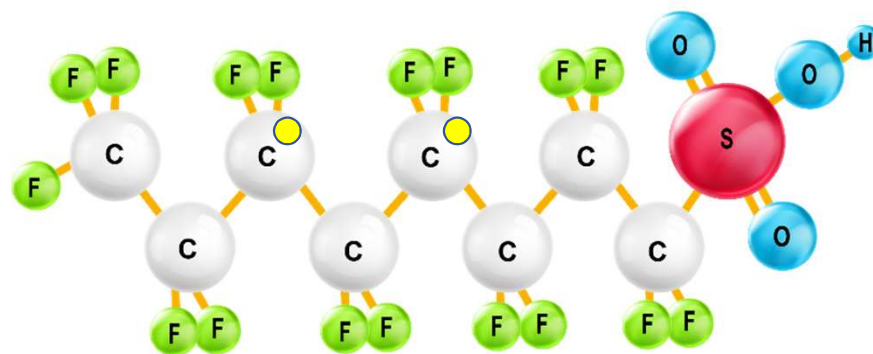
Atomic weight:
14.003241988(4) Da

Quantitation Technique: Isotopically-Labeled Standards

Atoms with the same number of protons, but different neutrons; e.g.,
Carbon-12, Carbon-13



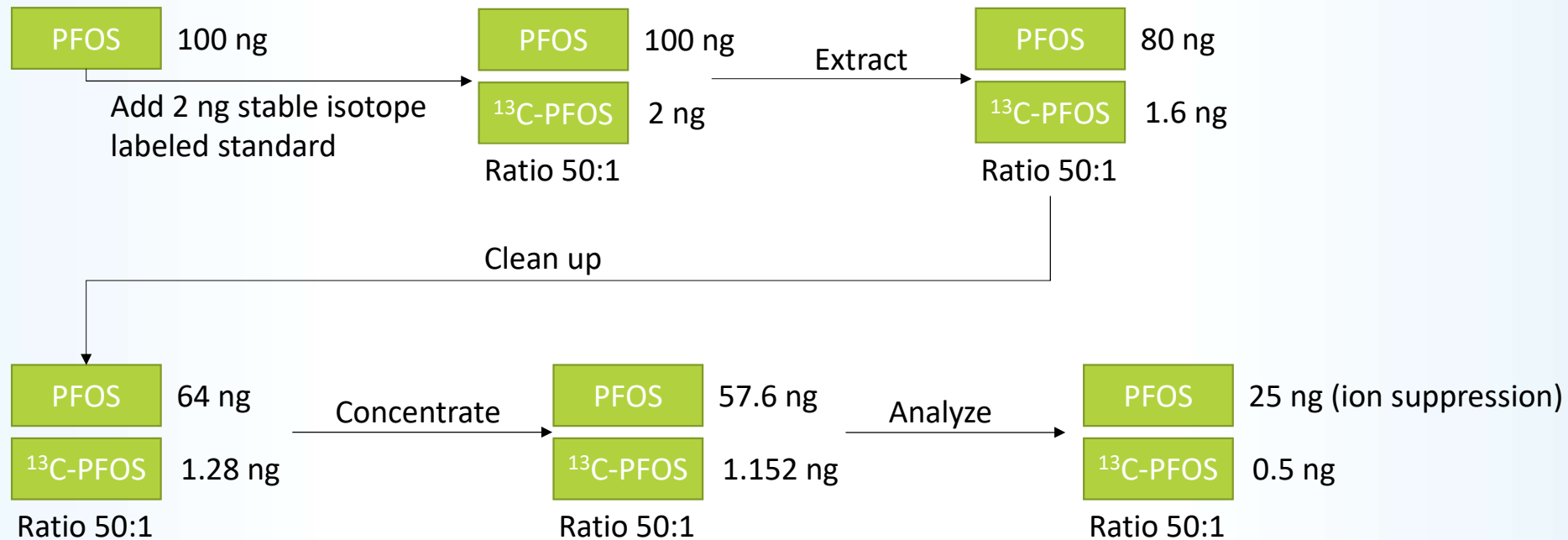
PFOS



$^{13}\text{C}_2$ -PFOS

It's a ratio game

Start Analysis



Without the labeled standard to track the losses and various effects, the measurement could be way off. With the stable isotope labeled standard, though, the ratio never changes. So measuring the ratio gives us great accuracy and precision.

ANALYTE	537	533
PFEESA		•
HFPOA-DA/Gen X	•	•
NFDHA		•
PFOS	4.5	5.47
PFUdA	•	•
N-MeFOSAA	•	
PFPeA		60.3
PFPeS		•
6:2 FTS		3.44
N-EtFOSAA	•	
PFHxA C6	35.9	69.0
PFDoA	•	•
PFOA	13.5	18.7
PFDA	1.51	2.03
PFHxS	1.74	2.35
PFBA		72.1
PFBS	27.1	35.4
PFHpA	11.7	18.6
PFHpS		•
PFNA	3.6	5.03
PFTeDA	•	
PFMOPrA		•
8:2 FTS		•
PFTTrDA	•	
9Cl-PF3PONS	•	•
4:2 FTS		•
11Cl-PF3OUds	•	•
PFMOBA		5.78
ADONA	•	•

But what about my previous data?

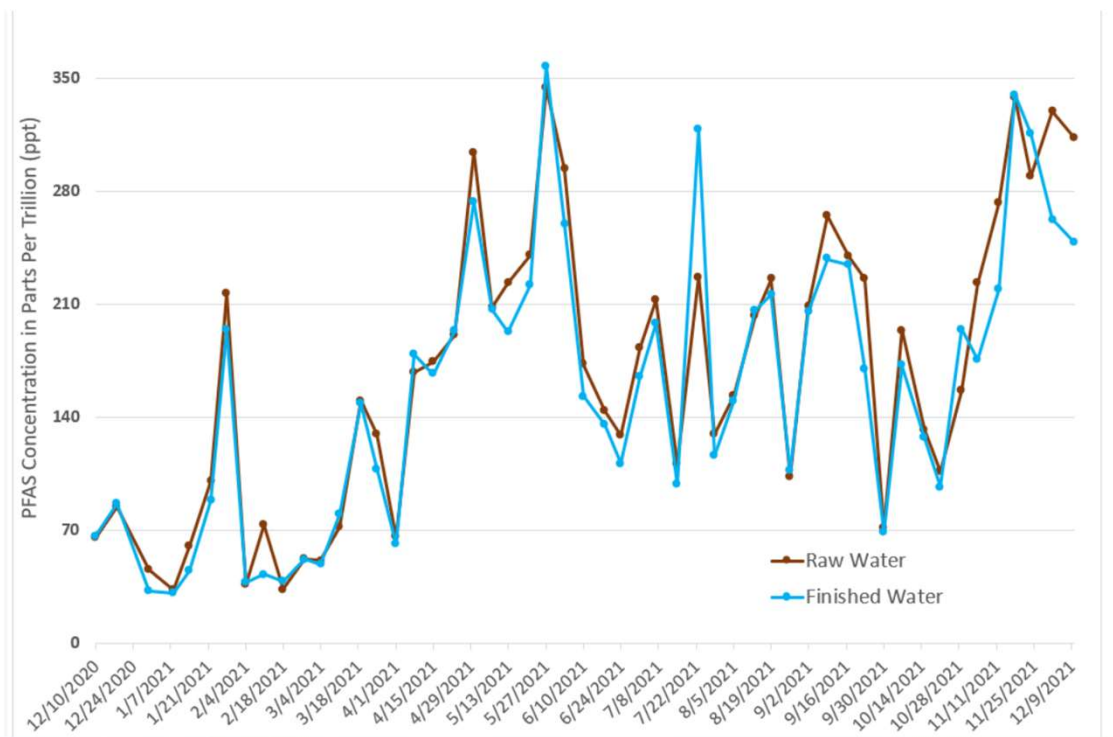
UCMR 5 Implications

- » Drinking water facilities will have to communicate to customers what these results or numbers mean
- » Know what your state regulations are if there is no regulations or recommendations in your state defer to EPA
- » Look at potential remediation options
- » Look for the source of the PFAS within their facility
- » But First...Set up a more thorough monitoring plan to validate that the numbers seen are representative of what is really present



Know your levels....

Study: Brunswick County tops national list for PFAS contamination



Numbers reported were a total of all PFAS tested.

When looking at the 70 ppt MCL of PFOA/PFOS combined

Brunswick County was well under. On average that total is 12 ppt.



Draft Method 1633 and its Implications



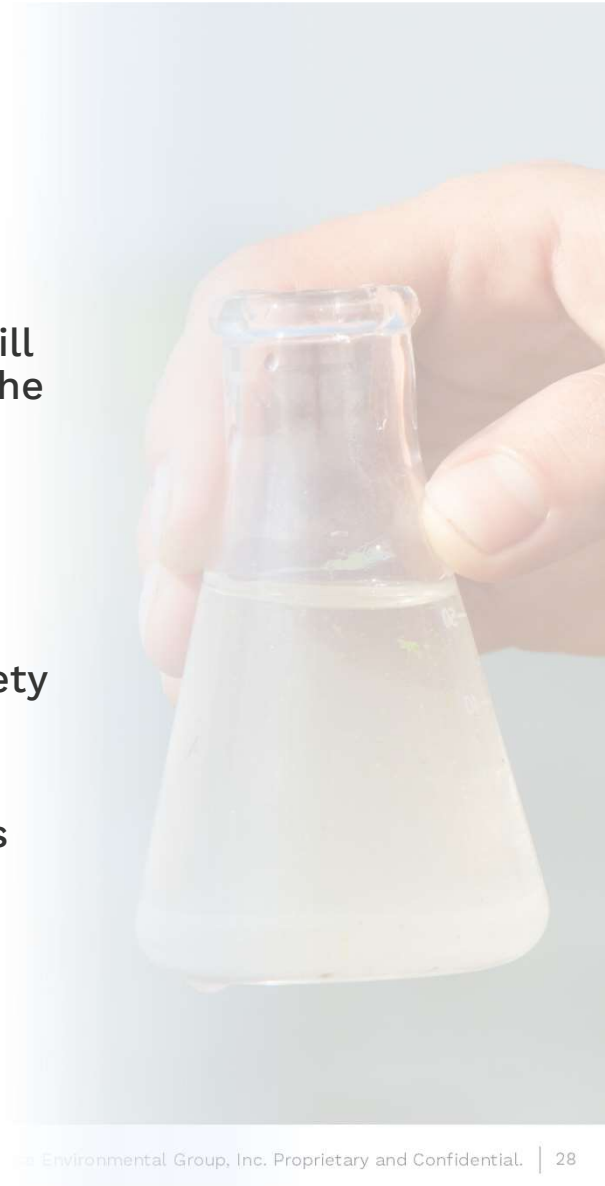
EPA Draft Method 1633

- » EPA/DOD combined effort
- » Draft Method 1633 published in September 2021
- » Issued 2nd Draft in June 2022
- » Matrices: eight different environmental media-- wastewater, surface water, ground water, soils, biosolids, tissues, leachate, and sediment
- » Single lab validation completed
- » Multi-lab validation in progress
- » Final Method expected this year



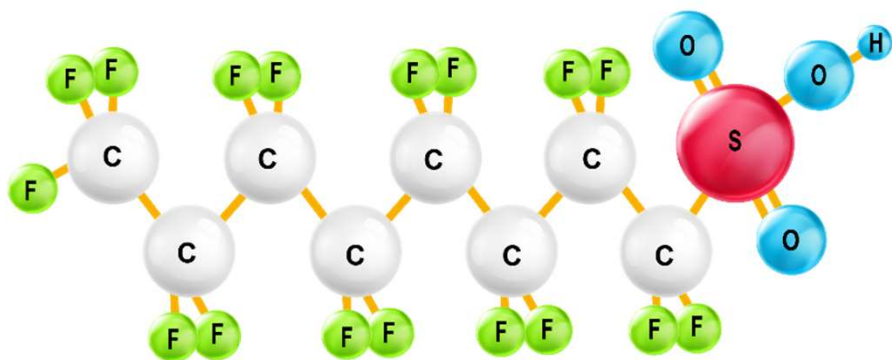
Implications of Draft 1633

- » Once EPA releases their non-drinking water method, WI DNR will change the WI DNR default PFAS list to match the 40 PFAS in the EPA method <https://dnr.wisconsin.gov/>
- » So current state lists might be updated to include all 40 PFAS...this might impact Drinking Water testing as well
- » **Will allow PFAS to be added to NPDES Permits**
- » Essentially allowable limits can be evaluated and set for a variety of matrices which impacts all facilities associated with those matrices....for example biosolids
- » Drinking water plants will now have an EPA method that allows them to identify the source of their PFAS
- » The same goes for waste water treatment plant

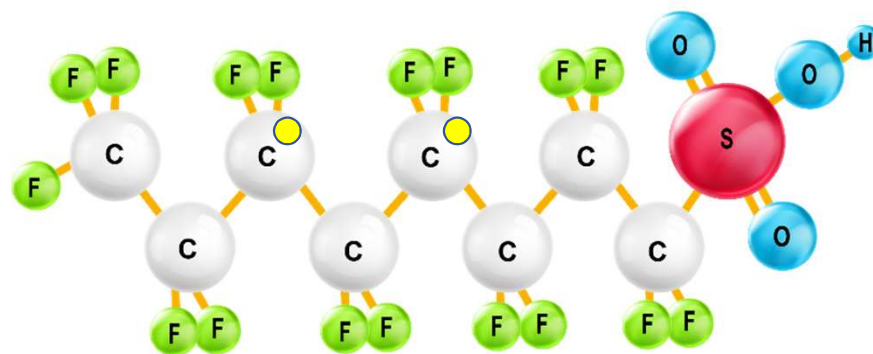


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PFOS



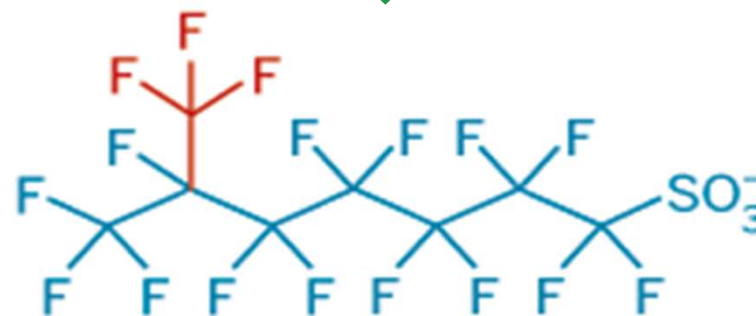
$^{13}\text{C}_2$ -PFOS

Linear and Branched Isomers

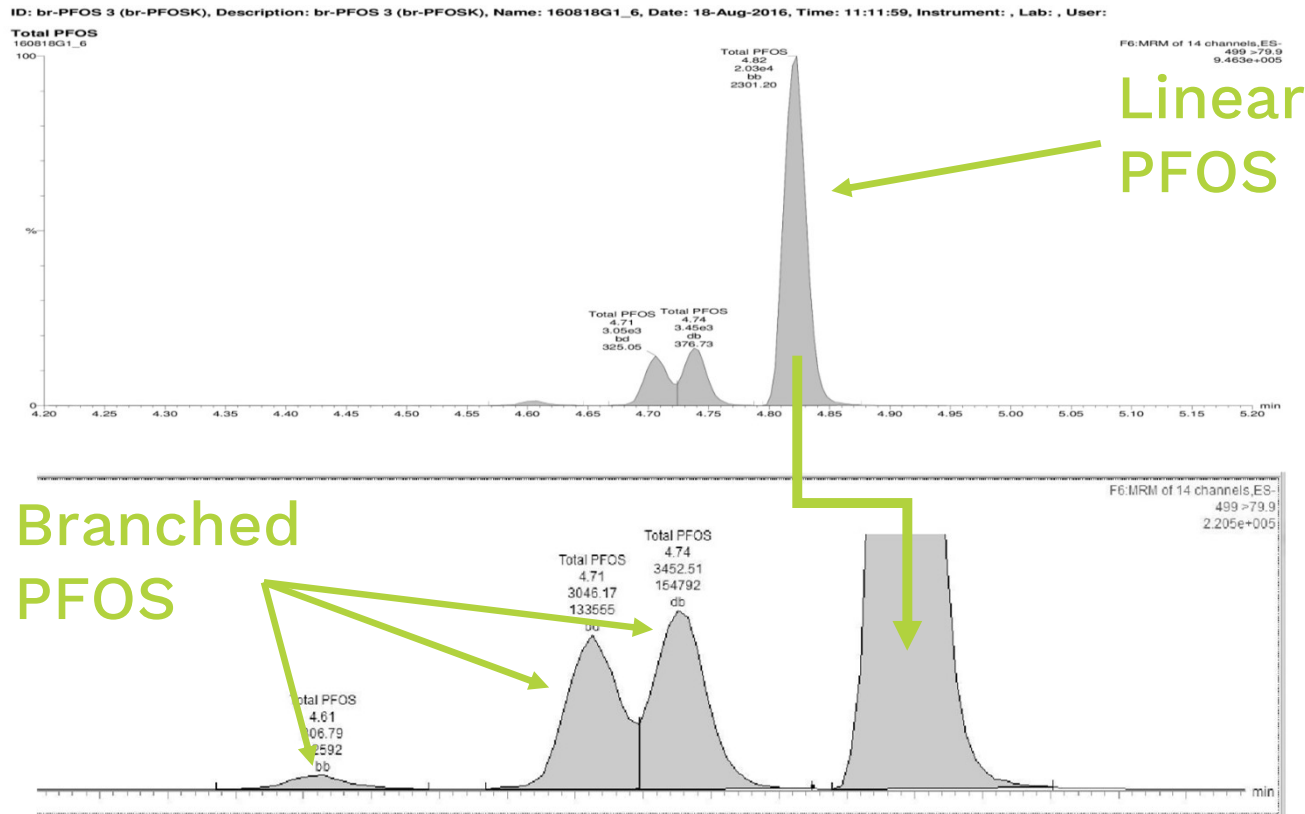
PFOS Linear Isomer



PFOS Branched Isomer



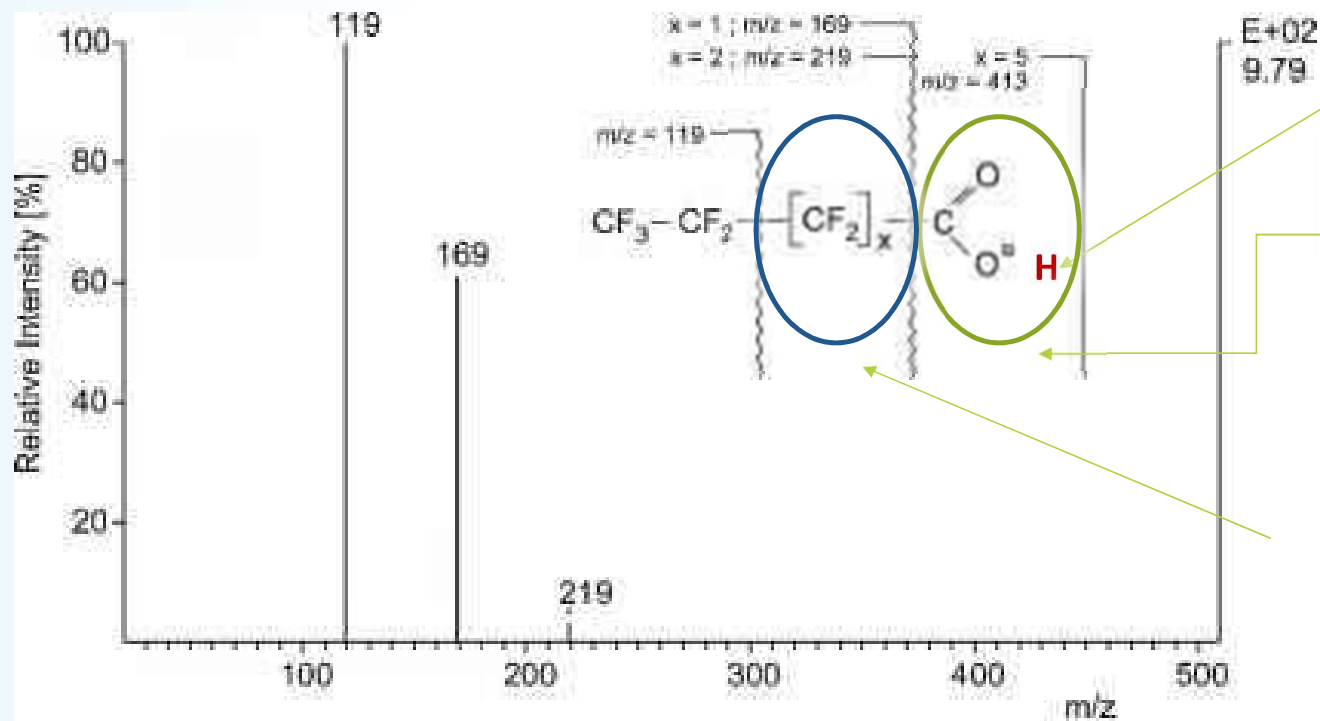
PFOS: Branched and Linear Isomers



Fragmentation Pattern of PFOA:

Longer Chain PFAS have more distinct fragments

PFOA has a molecular ion at 413 from a negative charged ion loss of one proton



first fragment is loss of CO₂
m/z 369

second fragment is 119 loss of CO₂
plus CF₂ X Chunk

Daily Quality Control

- » Instrument Blank
- » Instrument Sensitivity Check (3:1 S/N)
- » Calibration Verification
- » Qualitative Identification Standard (Branched/Linear)

- » Instrument Blank
- » Method Blank
- » Low-level OPR
- » Mid-range OPR
- » Bile Salt Interference Check Standard (if tissues will be included)
- » Ten or fewer samples
- » Calibration Verification
- » Instrument Blank

Some Good and some Bad...

» Positives...

- » Standardized analyte list
- » Relevant hold times
- » Data Comparability between labs
- » Performance-based procedures allow for improvements

» Negatives...

- » Added costs
 - » Excessive QC
 - » Labor intensive processes
 - » Analytically unnecessary requirements

Method Hold Times

Matrix	Hold Time		
	≤-20°C	0-6°C	
Aqueous	90 Days	28 Days	Issues observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamido acetic acids after 7 days.
Solid	90 Days	90 Days	May need to be extracted ASAP if NFDHA is an important analyte.
Tissue	90 Days	90 Days	May need to be extracted ASAP if NFDHA is an important analyte.

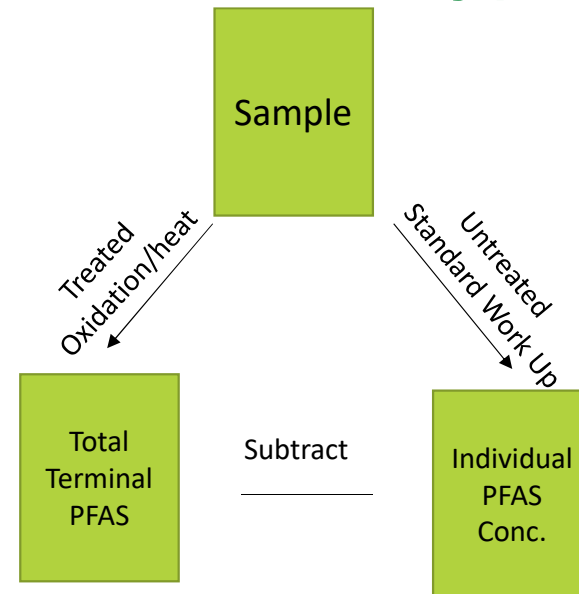
Other considerations for the lab

- » **Sample Matrix**
 - » any known contaminants / interferences?
 - » Is homogenization required?
 - » Chemically rich, i.e., leachate?
- » **Historical data?**
 - » Could this impact the instruments – and your data?
- » **Data requirements?**
 - » Target QLs?
 - » Report to QL or MDL?
 - » EDD format?

Communication is the key to success!

TOPS (Total Oxidizable Precursor Assay)

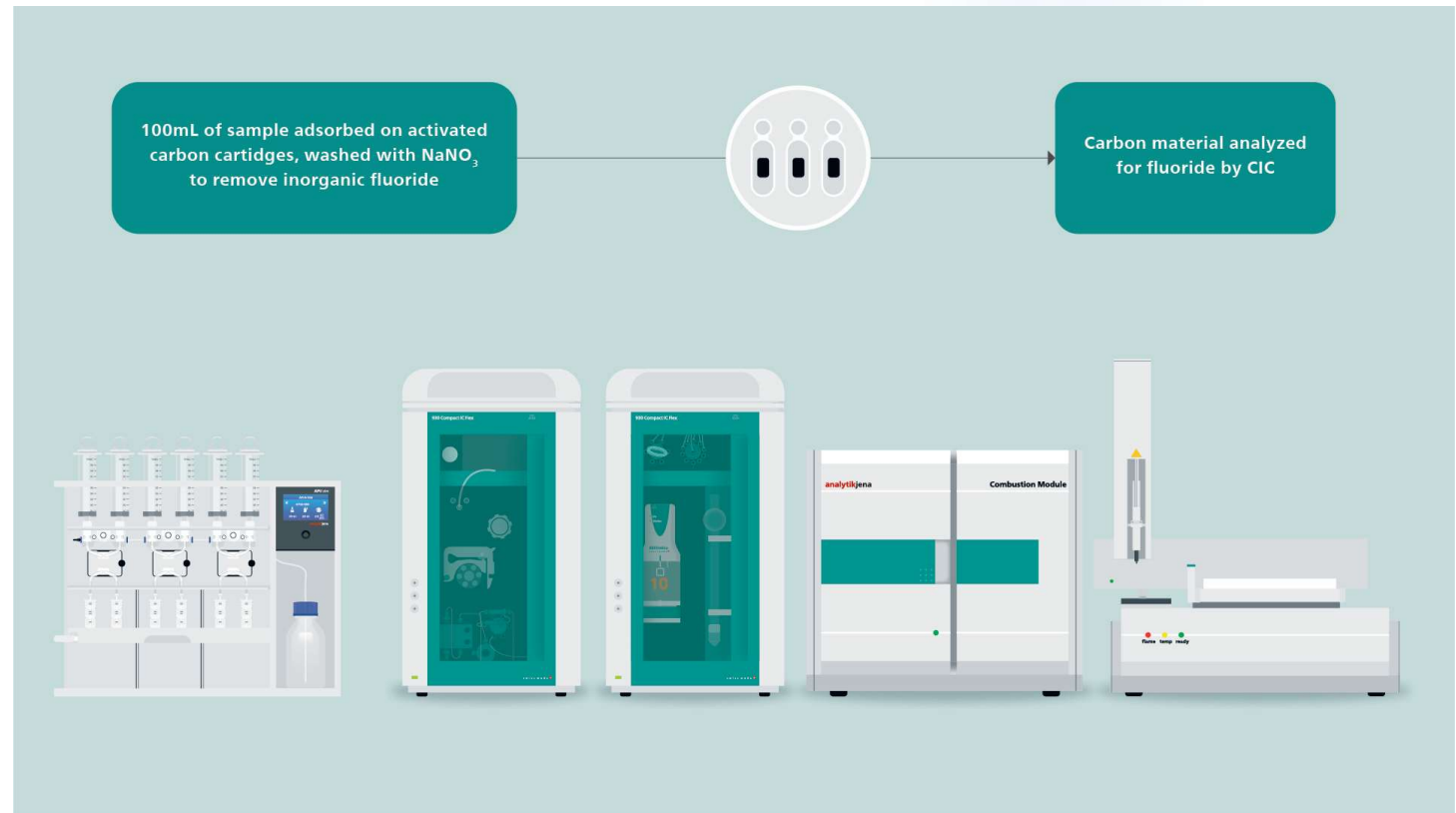
- Worst Case Estimate PFAS Composition
- Speeds up potential environmental oxidation that might occur over many years. Lab oxidation takes less than a day.
- Helpful in remediation testing as well as waste water treatment facilities.
- Used in AFFF analysis frequently.
- Assumptions are made-1) all non-targeted PFAS will be converted to targeted PFAS 2) 100% of the PFAS will be oxidized 3) all compounds oxidize similarly



The difference if any is presumed to be due to the oxidation of precursors

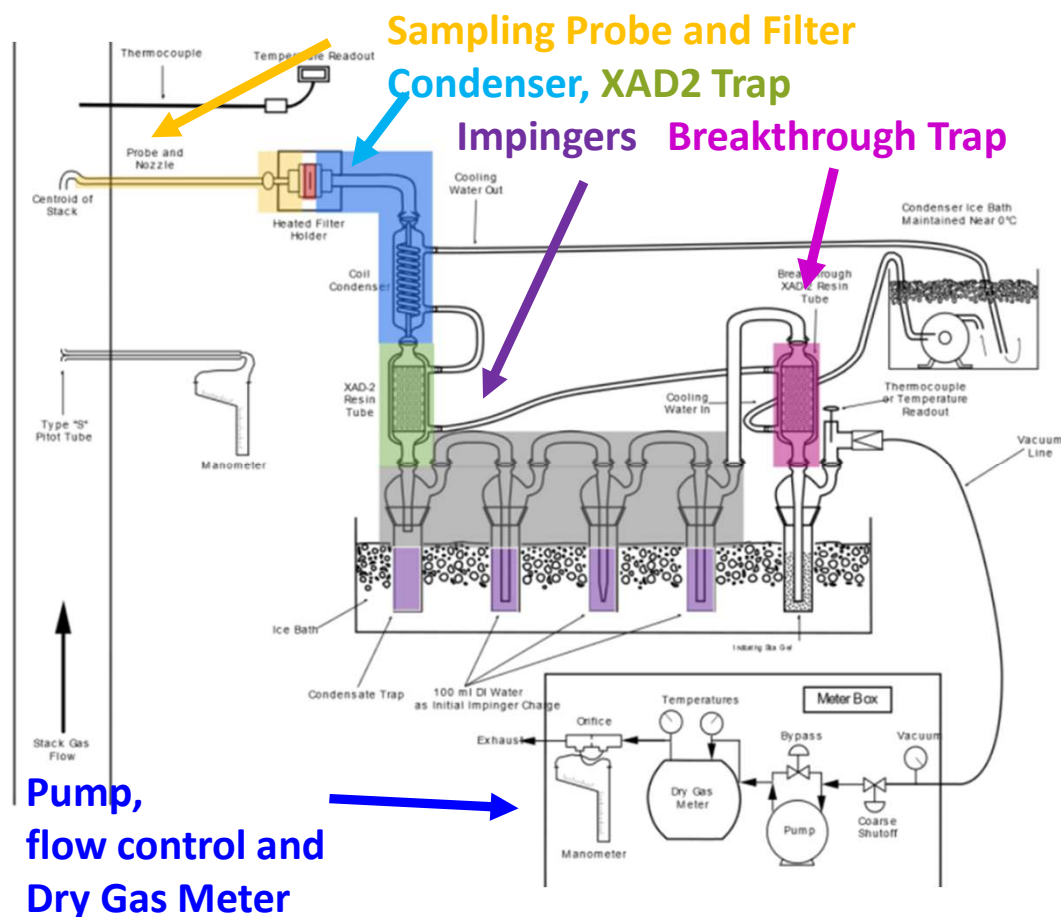
Draft EPA 1621 – AOF-CIC

- » Adsorbable Organic Fluorine by Combustion
- » Ion Chromatography
- » Aqueous Matrix Only
- » Results in ug/L range (ppb) for Organic Fluorine Only



Other Test Method 45(OTM-45) from EPA

- Probe inserted into the stack
- Pump draws stack gas sample through the apparatus or “train”
- Dry Gas Meter measures volume of dry stack gas sample drawn through train
- PFAS particles (or on particles) collected in the heated probe and filter
- PFAS in gaseous phase collected in ice-cooled XAD2 Trap and Impinger Water (bubbles through the water)
- Breakthrough Trap just in case
- Sample fractions recovered from each colored section in diagram (in field)
- Sample fractions sent to the Lab for extraction and Analysis



Questions?

JP Verheul

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» 804-467-1691





Sampling Techniques

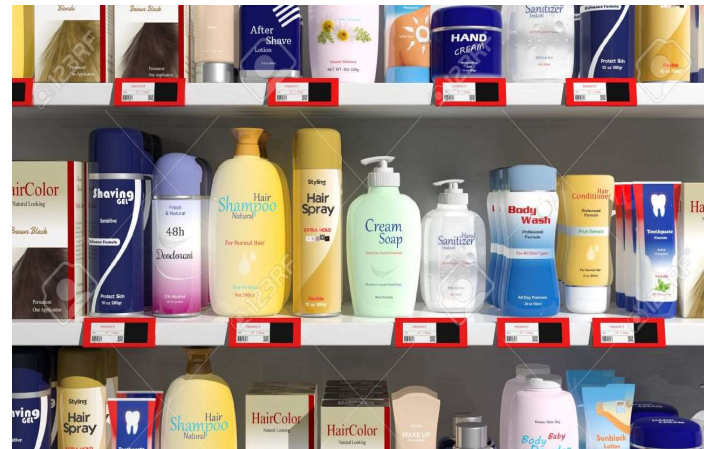


Common Sources of Laboratory Contamination

Samples should be collected in high density polyethylene (HDPE) containers pre-washed with methanol.

Common sources of laboratory contamination that should be avoided include:

- Aluminum foil
- Glass transfer pipettes
- Glass autosampler vials
- Vial caps with Teflon seals
- Pipette tips labelled as “low retention”
- Blue Ice



Your Outfit

What not to wear....

- Wear Clean Clothes
- Cotton Clothing
- Use Powder Free Nitrile Gloves
- Avoid Sunscreens, Make-up, and Lotions
- No Perfumes/Cologne
- No Dry Fit Clothing, Gortex, or Water-Proof Clothing
- Don't eat out there



Sampling Options

What questions am I looking to answer...

- Analytes to Measure
- Reporting Limits
- Trip Blank-prepped by lab
- Field Blank-prepared by you in the field
- Report Type



Grab Sampling

WWTP

- Use HDPE Containers Provided/Stainless Dipper
- Wash Hands and Wear Nitrile Gloves
- Pre-label with Ball Point Pen
- Waste Twice Then Collect
- Collect in Duplicate



USA Blue Book Part# 55295

Decontamination

PFAS Free Water (We can test your Milli Q/DI Systems)



Raw Water/Finished Water

Usually Clean Environment



Finished Water



Raw Water

Soils, Sediments, and Solids Sampling

NY Department of Environmental Conservation

- Acceptable equipment-Stainless Steel Spoon, stainless steel bowl, steel hand auger or shovel without coatings
- Decontamination-A 2 step process is most stringent. 1) detergent Alconox is acceptable 2) PFAS free water rinse
- Surface Soil 0-6 inches stainless steel spoon
- Shallow sub surface 6-36 inches dig hole with shovel then collect with pre-cleaned auger or spoon
- Sample should be placed in a stainless steel bowl and mixed by rolling the material in the middle until homogeneous. Then transfer to sample containers.
- Avoid contact with foil or PTFE.

Packing Your Sample

- What to do and extra precautions....
 - Place in Secondary Container (Zip Lock)
 - Use Wet Ice-Do Not Use Blue Ice
 - Can Refrigerate Until Shipped or Picked Up



- Can Bag Each Sample Location Separately
- We Can Supply Labeled Bags If You Like
- Can Bag Your Wet Ice
- Make Copies of Your COC

A Few Extras

What we have learned...

- Influent sampling is difficult
- True duplicates are tough
- Think about particulate
- Rotate your sampling schedule
- Think about nearby industries
- We can add analytes



Questions?

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