

SAME Environmental COI IGE Project Webinar: PFAS Sampling Considerations and Analytical Chemistry

June 23, 2022
1:00 PM EDT

HOUSEKEEPING NOTES & TIPS

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Submit a written question at any time via the “Q&A” tab. “Upvote” questions already asked to avoid duplication but indicate you also want an answer to that!

Click on the “Handouts” tab to download a copy of the presentation slides.

This webinar will be recorded for future viewing.

SPEAKERS



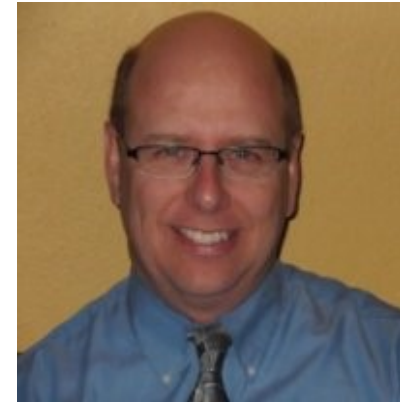
Moderator

Rick Wice, Battelle
SAME Chair for Environmental
Community of Interest (ECOI)



Speaker

Osaguona Ogbemor, DOE LLC
Professional Geologist with 28
years' environmental consulting
experience.



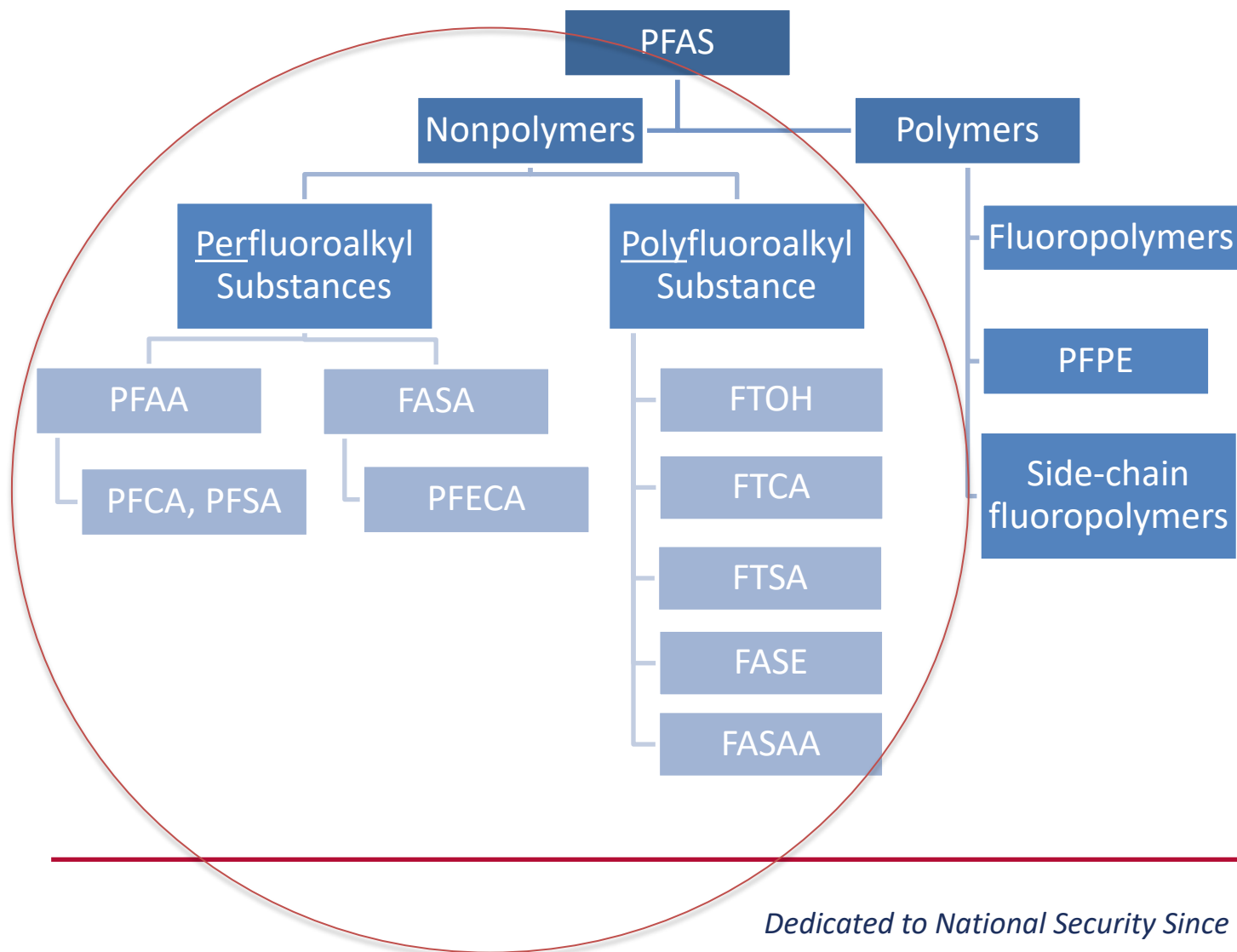
Speaker

John Powell, SIA Solutions
Chemist, Program Manager with 35
years' experience and PFAS Subject
Matter Expert.

AGENDA

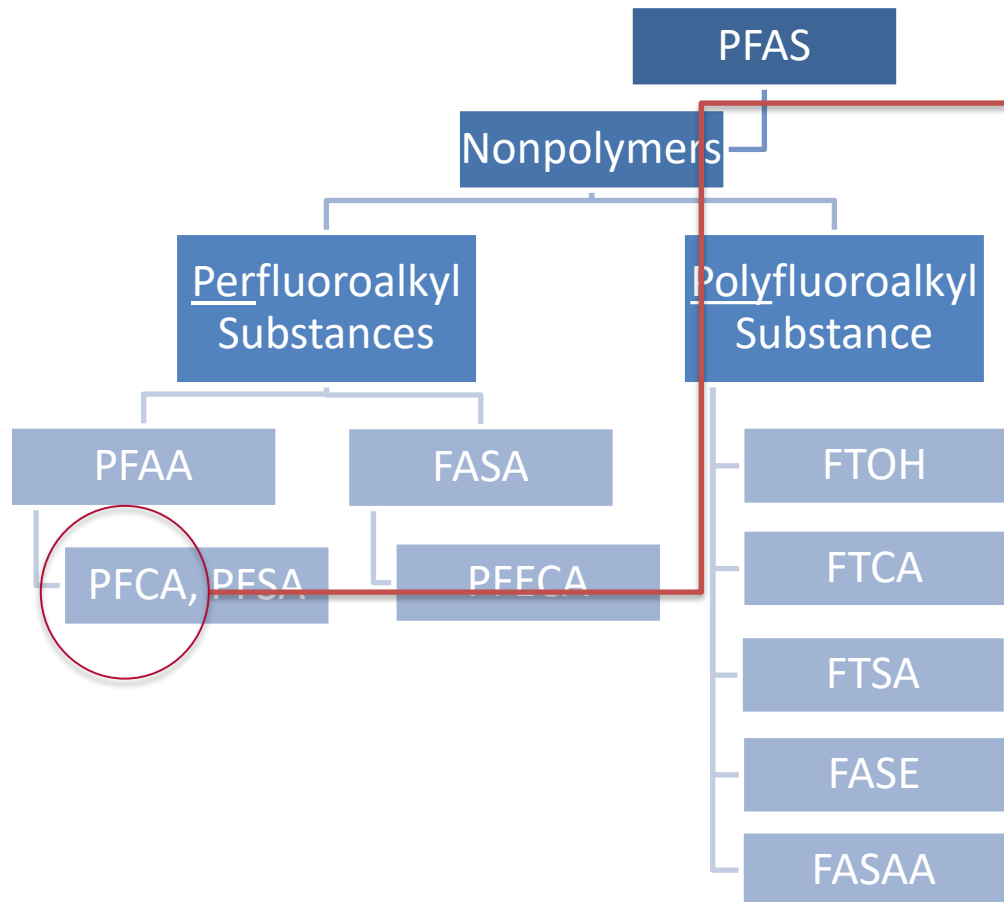
- Introductory information about PFAS chemistry
- Key elements that make PFAS sampling different from other sampling events
- Best practices for preparing for and conducting a PFAS sampling event
- Current state of PFAS analytical methods
- Basics of compound-specific PFAS analysis
- Alternative analytical techniques and how they can be useful

NOMENCLATURE



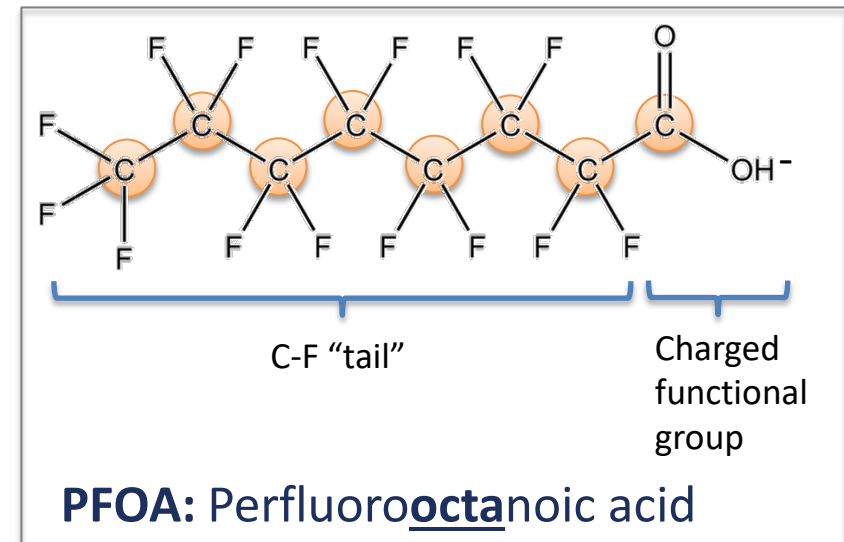
- PFAS are a family of >4,700 individuals arranged into a hierarchy of classes, subclasses, groups, and subgroups.
- When we talk about PFAS, we are usually talking about the **nonpolymer class** that are most commonly present in the environment.
 - Two most well known PFAS (PFOS and PFOA) are nonpolymers and perfluoroalkyl acids (PFAAs) specifically.
- Per- or Poly- is determined by whether each carbon is bonded only to fluorine.
 - Per = fully fluorinated
 - Poly = partially fluorinated

NOMENCLATURE



Individual PFAS are named based on the number of carbons in the chain.

- 4 carbons → buta → perfluorob**u**tanoic acid
- 8 carbons → octa → perfluoroo**o**ctanoic acid
- 10 carbons → deca → perfluorode**e**canoic acid



PFAA Naming System

- PFXY

- PF = perfluoro

- X = number of carbons

- Same convention as hydrocarbons
 - Includes C in the carboxylate group

- Y = functional group

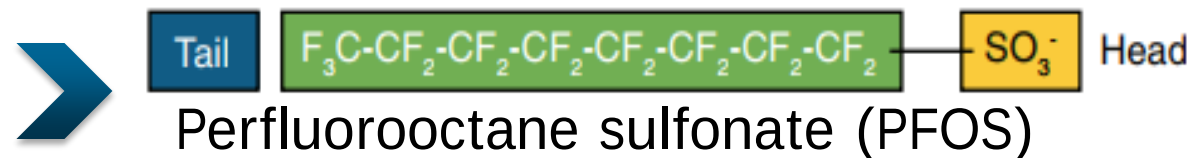
- S = sulfonate (R-SO₃⁻)
 - A = carboxylate (R-COO⁻)

4	B	(buta-)
5	Pe	(penta-)
6	Hx	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(nona-).....

- Example:

- X: 8 carbons = “octa”

- Y: S = sulfonate

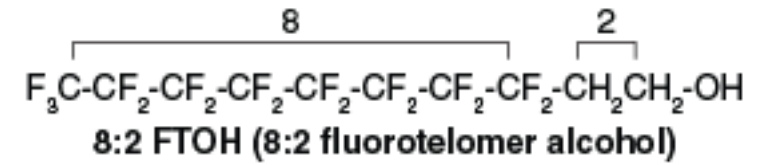


Which PFAA Are We Talking About?

- Acid or Anion?
 - PFAS may exist in various ionic states (acids, anions, cations, zwitterions)
 - In the environment, most PFAS exist in the anionic state (sulfonate, carboxylate, etc.)
 - Acid form of the name often used interchangeably (sulfonic acid and carboxylic acid)
 - Different CAS numbers & very different chemical and physical properties
- What Is My Lab Really Testing For?
 - Some labs report some or all of their PFAAs in the acid form
 - Depends on the standards used, which may be acids or salts of PFAAs (typically Na^+ or K^+)
 - The lab performs a calculation to account for the mass of the cation
 - For H^+ in acids, this is essentially irrelevant in terms of the results
 - For salts, confirm the lab is accurately accounting for the cation mass (Section 7.2.3 of EPA Method 537.1)

Polyfluoroalkyl Substances

- Partially fluorinated
- Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbons in the alkane chain



- Theoretically creates a “weak link” that may be susceptible to biotic or abiotic degradation
- Fluorotelomers are often named using a “n:x” prefix
 - n = number of fully fluorinated carbons
 - x = number of non-fully fluorinated carbons

PFAS Precursors (under environmental conditions)

- Some PFAS can degrade to PFAAs under environmental conditions
 - Referred to as “PFAA precursors”
 - Resulting PFAAs sometimes referred to as “terminal PFAAs”
- Perfluoroalkane sulfonamides (FASAs)
 - May degrade to PFSAs and PFCAs
- Polyfluoroalkyl Substances
 - Fluorotelomers
 - Fluorotelomer alcohols (FTOH)
 - Fluorotelomer sulfonates (FTS)
 - Fluorotelomer carboxylates (FTCA)
 - May degrade to PFCAs
 - Perfluoroalkyl sulfonamido-ethanols (FASE) & acetic acids (FASAA)
 - May degrade to PFCAs or PFSAs

As we learn more about transformation pathways, we may be able to use that information for site characterization – to determine sources, age, history, etc.

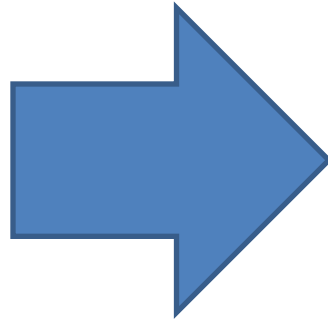
PFAS Sampling

General Sampling Guidelines

- Site-specific Quality Assurance Project Plan (QAPP) or work plan
- Refer to table on slide 16 for materials to avoid during sampling event
- Pretesting sampling equipment or materials
 - Equipment Rinse Blanks (ERBs/EBs)
 - Documentation during sampling event for any potential causes for bias

Sampling Event Preparation

The overarching objectives of the project and conceptual site model will influence the fundamentals of any sampling and analysis program



Develop a project-specific QAPP which addresses the increased risk of contamination and project-specific considerations

- Site history (e.g., potential sources, quantities used) as an indicator of potential level of PFAS
- Project Action Levels

- Project team must discuss with the laboratory:
 - the PFAS to be analyzed and project reporting levels,
 - the volume of sample required to achieve the lab reporting levels,
 - project sample preparation requirements, and
 - the number of bottles needed, including QC samples.
- Provide laboratory information on high concentration samples
- For Draft 1633 request laboratory screen all samples prior to sample preparation (additional containers for aqueous samples needed)

Equipment & Supplies

- There are some materials that should be avoided due to contamination and possible adsorption issues that if used and contacted sample may introduce bias
 - polytetrafluoroethylene (PTFE)
 - waterproof coatings containing PFAS
 - fluorinated ethylene-propylene (FEP)
 - ethylene tetrafluoroethylene (ETFE)
 - low-density polyethylene (LDPE) [adsorption]
 - polyvinylidene fluoride (PVDF)
 - pipe thread compounds and tape

Equipment & Supplies

Prohibited Materials and Equipment	Recommended Material and Equipment
Teflon® containing or coated field equipment (tubing, bailers, tape and plumbing paste)	HDPE and silicon Materials include tubing, bailers, tape, plumbing paste
Teflon® lined lids on containers (for example sample containers, rinsate water storage containers)	Polypropylene lids ³ for sample containers and polypropylene or HDPE containers for rinsate
Glass sample containers with lined lids	Use polypropylene or HDPE for sample containers ³ (PFAS adsorb strongly to glass).
Aluminium foil	Thin HDPE sheeting (commonly used as drop cloths for painting or home improvement) can be used.
Self-sticking notes and similar office products (for example 3M Post-It notes)	Avoid the use of these products at the site.
Drilling fluid containing PFAS	PFAS-free drilling fluids or use alternative techniques (for example sonic drilling) which do not require drilling fluids
LDPE or polypropylene containing materials (e.g., bags or containers used to transport samples)	Acetate liners for direct push technologies
Paper products such as waterproof field books, plastic clipboards, binders, spiral hard cover notebooks, sticky notes or glue materials	Loose paper with Masonite or aluminum clipboards
Markers	Pens
Chemical (blue) ice packs	Ice contained in plastic (polyethylene) bags (double bagged).
Decontamination soaps containing fluoro-surfactants such as Decon 90	Alconox® or Liquinox®
Water that is not verified to be “PFAS-free” to be used for trip and decontamination blanks and decontamination processes	Laboratory supplied and verified “PFAS-free” water to be used for trip and decontamination blanks and decontamination processes
Water resistant, waterproof, stain-treated clothing or shoes including Gore-Tex™ and Tyvek® materials	Cotton construction is recommended for field clothing and should be laundered a minimum of 6 times from time of purchase due to possible PFAS related treatments. Fabric softener must be avoided. Rain gear should be made from polyurethane and wax-coated materials
	Nitrile gloves – change often

Equipment & Supplies

- Review Safety Data Sheets (SDS); if PFAS listed, recommendation to not use
 - Exclusion from SDS does not assure PFAS are not present in equipment/material
- Conservative sampling approach is best
- Tiered approach
 - 1st: Restrictions on sampling materials in direct contact with samples
 - 2nd: Restrictions on materials allowed on personnel and staging area

What To Do If You Are Unsure If Item Contains PFAS Or Not?

- Review the Safety Data Sheets and consult with the manufacturer of the item
- Consult:
 - PFAS sampling guidance documents
 - PFAS resources within your organization
 - An analytical chemist with PFAS experience
- Collect equipment blank(s) from a specific item in question or send a section or piece of the equipment (if practical) to the laboratory for a more vigorous leachate analysis

Sample Container Selection

- Specific requirements based on analytical method
- USEPA 537.1
 - polypropylene containers and caps/lids for drinking water sampling
- USEPA 533
 - allows for the use of polypropylene or polyethylene containers and polypropylene caps/lids for drinking water sampling
- USEPA SW-846 Method 8327
 - validated using polypropylene containers for groundwater, surface water, and wastewater sampling
 - other types of containers such as high-density polyethylene (HDPE) may be used if the needs of the project can be met with their use
- USEPA Draft 1633
 - requires the use of HDPE containers for wastewater, groundwater, surface water, landfill leachate, biosolids, soil, sediment, and tissue sampling
 - requires a second container for screening aqueous samples

Sample Considerations

- USEPA Methods 537.1 and 533, and USEPA Draft Method 1633 all require the laboratory to prepare the entire sample collected, including sample container rinsate(s)
- DoD AFFF01 requires the container holding the diluted AFFF concentrate be prepared in its entirety, including a rinse of the container

Laboratory Supplied Sampling Materials

Sample containers (polypropylene or HDPE), solvents (such as methanol), and water used for blanks in the field and for final rinse of equipment should:

- be supplied by the lab performing the analysis, and
- be verified as being PFAS-free (as defined by the project) prior to use

If site water is used in the field for any blanks or final rinse, a sample of this water should be sent to the laboratory for analysis.

Sample Preservation, Shipping, Preservative

- Differences for each analytical method
- Method specific info – 537.1, 533, 3512/8327, 1633
- USEPA 537.1 Triz (Trizma)
- USEPA 533 ammonium acetate

Sample Hold Times

Method	Extraction	Analysis
USEPA 537.1	14 days	28 days
USEPA 533	28 days	28 days
SW-846 3512/8327	14 days	30 days
USEPA Draft 1633 (refrigerated)	28 days*	28 days*
USEPA Draft 1633 (frozen)	90 days*	90 days*

- *multiple caveats; please see Method for exceptions

Field Decontamination

- Reusable field equipment cleaned between samples
- The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluorosurfactants are not listed as ingredients
- Heavy equipment best cleaned at decontamination facility or other containment method
- Use laboratory-verified PFAS-free water in final rinse of decontamination of sampling equipment

Field Quality Control

- USEPA 537.1 and 533 have additional requirements
 - Minimum of one field reagent blank for each set of samples per site and field duplicates
 - Both methods specify the frequency of the field duplicate in terms of extraction batch (one per extraction batch, not to exceed 20 field samples), not collection frequency
- Additional quality control samples may be needed based on site-specific work plan and data quality objectives

QA/QC Sample Collection

Using blanks to evaluate composition or suitable nature of equipment/supplies for sampling, and to assess possibility of cross-contamination during sampling/transport/storage

- **Pre-investigation equipment blanks** (decon water, methanol, new equipment, plastic bags as sample containers, anything you are unsure of)
- **Equipment blanks** to assess adequacy of decontamination process and/or evaluate potential contamination from equipment.
- **Field blanks** to assess contamination from field conditions.
 - Recommended frequency: one blank/day/matrix or one blank/20 samples/matrix, whichever more frequent.
 - **Field reagent blanks** (USEPA Method 537.1, 533) should originate from the laboratory for all drinking-water programs (minimum of 1/event).

Draft Other Test Method 45 (OTM-45)

- USEPA 2021 *Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources*
- Sample and analyze PFAS targets from stationary sources
- Additional field QC measures such as field blanks, isotopically labeled PFAS field spikes

Filtering of Water Samples

- Evidence that PFAS may sorb onto various filters (e.g., glass fiber filters)
- Data may be misinterpreted as PFAS sorbed to soil or sediment in the water sample when the reduction may actually reflect PFAS sorbed onto the glass fiber filter
- Consider use of low flow sampling
- Laboratory centrifugation is a good alternative

- Special considerations for PFAS sampling – what matters is what comes into contact with sample, have a practical approach to contamination concerns
- Method specific requirements for sampling, sample preservation, shipping & holding times varies
- PFAS-specific sampling protocols are recommended – general guidelines exist
- Sample event planning/upfront work is key

PFAS Analysis

USEPA PFAS Drinking Water Methods

- USEPA 537.1
 - Finalized Method (Version 2.0 published 2020)
 - Compound-Specific Analyses (18 PFAS)
- USEPA Method 533
 - Finalized Method (published 2019)
 - Compound-Specific Analyses (25 PFAS)
 - Addresses some compounds that were not included in Method 537.1 due to poor performance

USEPA PFAS Drinking Water Methods

- USEPA Method 537.1 & 533 Similarities
 - Sample preparation via Solid Phase Extraction (SPE)
 - Compound-Specific Analysis by LC-MS/MS
 - Laboratories allowed some modifications, but not:
 - Sample collection/preservation
 - Extraction
 - Quality control
 - Multi-laboratory validated method

USEPA PFAS Drinking Water Methods

- USEPA Method 537.1 & 533 Differences
 - Sample collection - chemical preservation
 - Analysis
 - Compound-Specific Analysis by LC-MS/MS
 - Quantification scheme
 - Analyte Lists

USEPA PFAS Drinking Water Methods

Method 537.1 Only		Both Methods 537.1 and 533			Method 533 Only		
NEtFOSAA	NMeFOSAA	PFOA	PFOS	11Cl-PF3OUdS	4:2 FTS	6:2 FTS	8:2 FTS
PFTA	PFTrDA	PFDA	PFDoA	9Cl-PF3ONS	PFBA	PFHpS	PFPeS
		PFHxA	PFUnA	ADONA	PFPeA	PFMBA	PFMPA
		PFBS	PFHpA	HFPO-DA	PFEESA	NFDHA	
		PFHxS	PFNA				

USEPA Draft Method 1633

- Draft published USEPA Method 1633
 - Single-laboratory validated August 2021
- Isotope dilution method
 - Compound-Specific Analyses (targeting 40 PFAS)
 - GW, SW, WW, Leachate, Biosolid, Tissue, Sediment, Soil

USEPA Draft Other Test Method 45 (OTM-45)

- January 2021
 - Single-laboratory validated
- Compound-Specific Analyses by LC-MS/MS (50 PFAS analytes)
- Semivolatile and nonvolatile polar PFAS in air emissions (stationary sources)
- Includes sampling, sample preparation, and analytical procedures

SW-846 Method 8327

- July 2021
- Compound-Specific Analyses by LC-MS/MS (24 PFAS analytes)
 - Does not include all PFAS included in USEPA Method 537.1 or 533
- GW, SW, and WW
- DoD has determined that this method is not capable of achieving required quality objectives therefore, DoD considers this a screening method. Method 8327 should not be used for collection of definitive data.

DoD AFFF01

- December 2021
 - Multi-laboratory validated
- LC-MS/MS (PFOA and PFOS only)
- AFFF concentrates
 - Compliance for military specifications MIL-PRF-24385

Other published methods

- Finalized Methods
 - ISO Method 25101 (ISO 2009)
 - ASTM D7979-20 (ASTM 2020)
 - ASTM D7968-17a (ASTM 2017)
 - FDA C-010.01 Version 2019
 - CDC:6304.09
- Draft Methods
 - ISO/CD 21675:2019 (E)

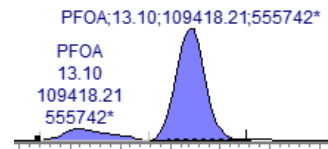
Key Method Differences

- Method Scope
 - Media
 - Limit of Detection & Quantitation
 - Analytes (individual and isomeric profile)

Branched & Linear PFAS

- PFAS from ECF chemistry: $\sim 22 \pm 1.2\%$ branched and $78 \pm 1.2\%$ linear isomer¹
- Branched and linear isomers of PFAS (including PFCAs) produced by ECF seen in consumer products, groundwater, sediment, soil, wastewater, landfills
- Observing branched isomers depends on chromatography

branched isomers-
10 co-eluting in
single peak



linear isomer

- If ignoring the branched peak, concentrations may be biased low by $\sim 25\%$
- Telomer chemistry theoretically produces predominantly linear PFAS, however, final product may contain branched isomers.

Key Method Differences

- Sample preparation processes
 - Whole sample vs Aliquot
 - Solid Phase Extraction vs solvent dilution
- Clean-up vs no clean-up
- Quantitation Scheme
 - External standard
 - Internal standard
 - Isotope standard quantitation

Data Review and Validation

- Published Data Review and Validation Guidelines
 - Drinking Water Data Validation Guidance (*Data Review and Validation Guidelines for Perfluoralkyl Substances (PFASs) Analyzed Using EPA Method 537* (EPA 910-R-18-001, November 2018)
 - Data Review Guidance (USEPA Technical Brief “Per-and Polyfluoroalkyl Substances (PFAS): Reviewing Analytical Methods Data for Environmental Samples.” April 2019)
 - DoD Validation Guidance (*Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-15*, May 1, 2020) (<https://www.denix.osd.mil/edqw/index.html>)

Less-Standardized Analytical Techniques

- Particle-Induced Gamma Emission (PIGE) spectroscopy measures elemental fluorine from a sample isolated on a thin surface
- Precursor Analysis by Total Oxidizable Precursor (TOP) Assay measures PFAA precursors or polyfluorinated compounds that can be converted to PFAAs
- LC quadrupole time-of-flight mass spectrometry (LC-QToF-MS) tentatively identifies PFAS structures through library matches (non-targeted analysis)
- Extractable/Absorbable Organic Fluorine (EOF/AOF) measures fluorine in a sample as fluoride

- There are a number of PFAS analytical methods published
- Significant differences between methods need to be evaluated when selecting a method in order to achieve project's DQOs.
- Additional analytical methods are currently in development
- Less-standardized analytical techniques can be helpful as a qualitative, or screening tool.