25th Annual New England Pretreatment Coordinators Workshop
October 25-26, 2023
Sheraton Nashua
Nashua, NH

Overview of PFAS Analytical Methods 1633 & 1621

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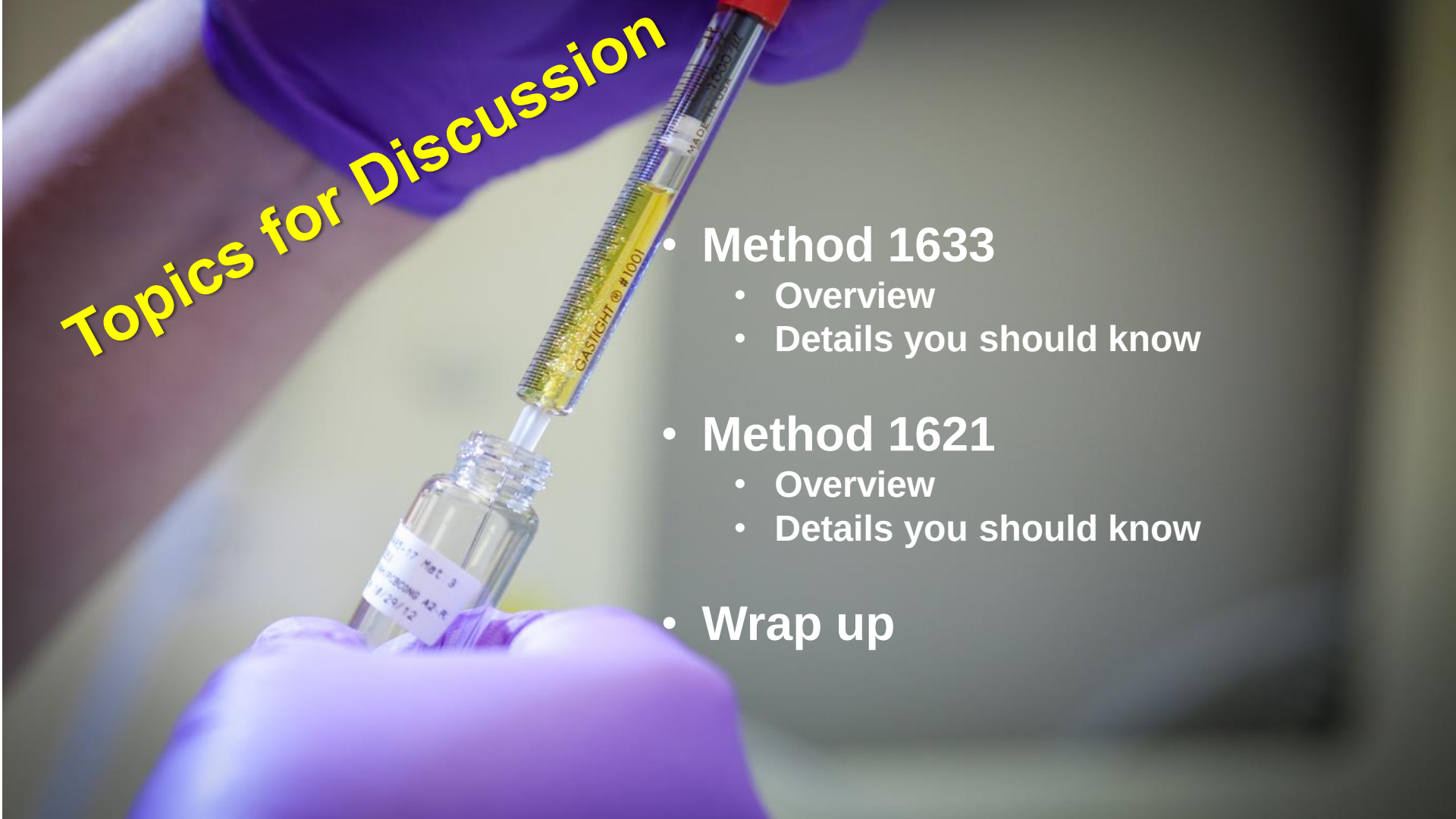


- **Method 1633**
  - Overview
  - Details you should know
- **Method 1621**
  - Overview
  - Details you should know
- **Wrap up**

THE PFAS LIFECYCLE

- Industry is the most common source of PFAS contamination - both the manufacturers of PFAS chemicals and those that use them in the products they make
- Perfluorinated PFAS are very persistent & Polyfluorinated PFAS can transform into perfluorinated PFAS in the environment

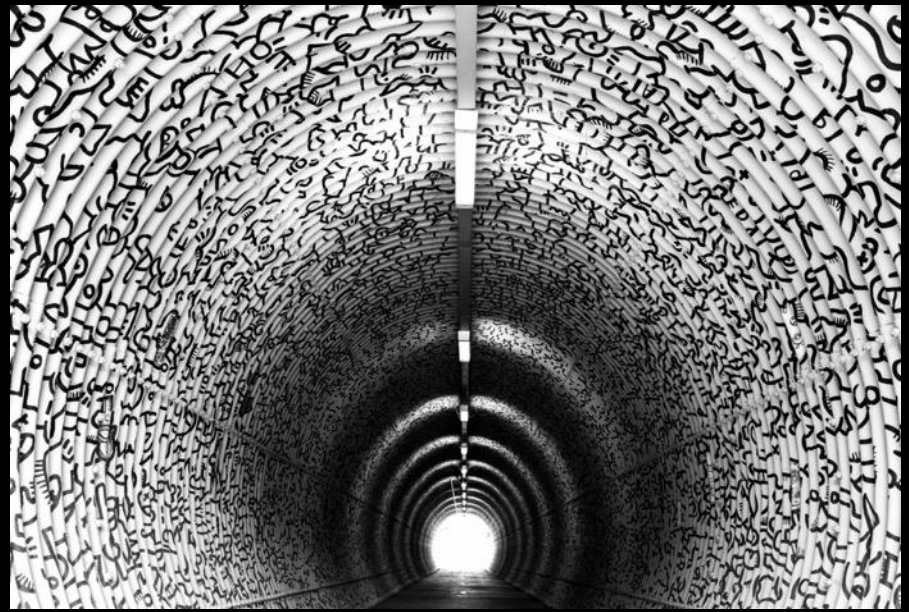
- Textile manufacturing
- Certain paper food wrapping
- Metal plating & etching
- Wire manufacturing
- Pesticides
- Personal care products
- Non-stick cookware

Department of Defense and other users of AFFF (Aqueous film forming foam)

Especially if unlined, such as those used for construction and demolition debris

Can convert PFAS precursors into PFOA and other PFAAs

Over half of the sludge produced in the US is land-applied as biosolids and may introduce PFAS into the food chain



Draft Method 1633 – Can we finally see the light at the “end of the tunnel”?

3 New EPA SW-846 Methods Proposed

- (1) Non-potable water: SW-846 Method 8327 draft, fall 2018
  - LC/MS/MS direct injection, external standard calibration
  - 24 analytes
- (2) Non-potable water: SW-846 Method 8328
  - LC/MS/MS SPE , isotope dilution
  - 24 analytes
- (3) Solids: SW-846 Method 8329 TBD

early 2018 vintage slide

late 2018 vintage slide

Additional EPA Methods?

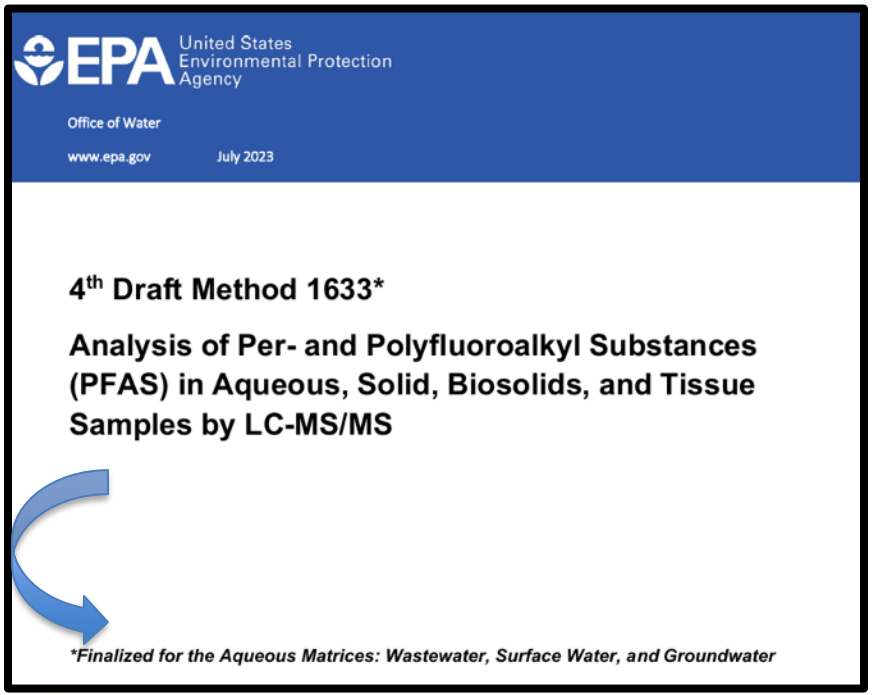
- SW-846 Method 8328 Target date??
  - Non-potable water plus soils, sediments & biosolids
    - LC/MS/MS SPE, isotope dilution
    - 24 analytes plus HFPO-DA
    - Consistent with DoD QSM 5.1, Table B-15
- EPA 1600 series method?
  - EPA working with DoD
- ~ 40 compounds?

Draft Method EPA 1633

- EPA announced the method Sept 2021
- **Eight matrices** - wastewater, surface water, groundwater, soils, biosolids, tissue, leachate, and sediment
- Multi-lab study completed 2022; EPA working on revisions to incorporate the results, **3 prior draft releases**
- **Draft 4 released in July**
- Method 1633 being added to certain state NPDES permits and some municipal landfill groundwater programs

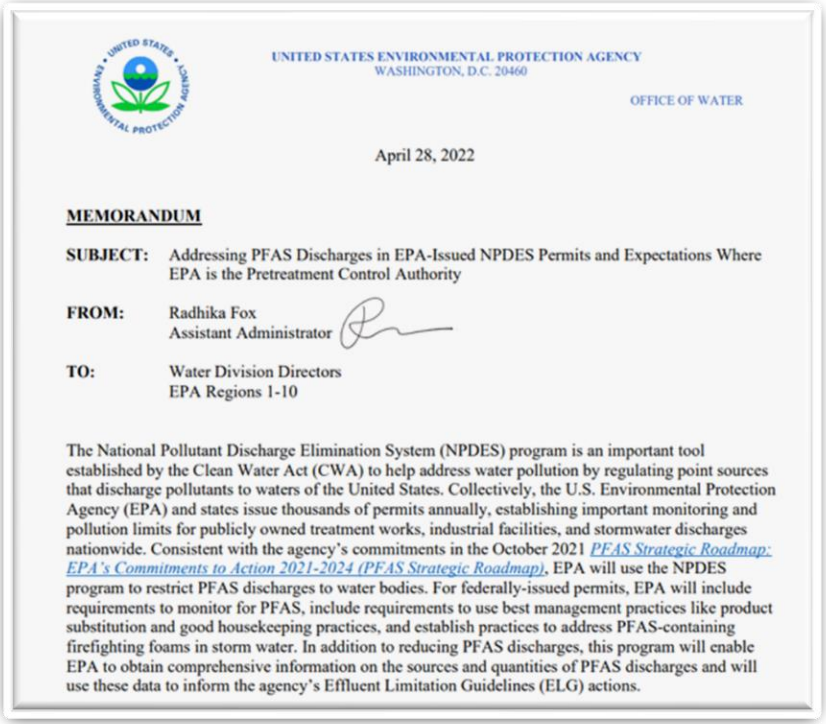
Image copied from: Cincinnati Enquirer

Draft vs. Final Methods



- **DRAFT methods are single lab validated**
- **FINAL Methods are multi-lab validated**
- **AQ matrix finalized in Rev 4, multi-lab validation study ongoing for solids & tissues**
- **Implications of *"half-final" status*?**

Effluent-monitoring: In the absence of a final 40 CFR § 136 method, use Clean Water Act (CWA) wastewater draft analytical method 1633. (See 40 CFR 122.21(e)(3)(ii) and 40 CFR 122.44(i)(1)(iv)(B)). Monitoring should include each of the 40 PFAS parameters detectable by draft method 1633…



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

April 28, 2022

MEMORANDUM

SUBJECT: Addressing PFAS Discharges in EPA-Issued NPDES Permits and Expectations Where EPA is the Pretreatment Control Authority

FROM: Radhika Fox
Assistant Administrator

TO: Water Division Directors
EPA Regions 1-10

The National Pollutant Discharge Elimination System (NPDES) program is an important tool established by the Clean Water Act (CWA) to help address water pollution by regulating point sources that discharge pollutants to waters of the United States. Collectively, the U.S. Environmental Protection Agency (EPA) and states issue thousands of permits annually, establishing important monitoring and pollution limits for publicly owned treatment works, industrial facilities, and stormwater discharges nationwide. Consistent with the agency's commitments in the October 2021 *PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024 (PFAS Strategic Roadmap)*, EPA will use the NPDES program to restrict PFAS discharges to water bodies. For federally-issued permits, EPA will include requirements to monitor for PFAS, include requirements to use best management practices like product substitution and good housekeeping practices, and establish practices to address PFAS-containing firefighting foams in storm water. In addition to reducing PFAS discharges, this program will enable EPA to obtain comprehensive information on the sources and quantities of PFAS discharges and will use these data to inform the agency's Effluent Limitation Guidelines (ELG) actions.

Method 1633 Target Compound List

Target Analyte Name	Abbreviation	CAS Number
Perfluoroalkyl carboxylic acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluoroalkyl sulfonic acids		
Acid Form		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentansulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Fluorotelomer sulfonic acids		
1*H*,1*H*, 2*H*, 2*H*-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4
Perfluorooctane sulfonamides		
Perfluorooctanesulfonamide	PFOSA	754-91-6
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2
Perfluorooctane sulfonamidoacetic acids		
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
Perfluorooctane sulfonamide ethanols		
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2
Per- and Polyfluoroether carboxylic acids		
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
4,8-Dioxa-3*H*-perfluorononanoic acid	ADONA	919005-14-4
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6

Target Analyte Name	Abbreviation	CAS Number
Ether sulfonic acids		
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7
Fluorotelomer carboxylic acids		
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	5:3FTCA	914637-49-3
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4

Fluorotelomer carboxylic acids	
3-Perfluoropropyl propanoic acid	3:3FTCA
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	5:3FTCA
3-Perfluoroheptyl propanoic acid	7:3FTCA

Parameter	Draft #2	Draft #3	Draft #4
Sample Collection	Section 8.2.3 was changed for storage options of aqueous samples	No Change	No Change
	section 8.3.2 was changed for soil storage options	Added info about sufficient ice	No Change
Materials	No change	GCB cartridges allowed for wastewater	GCB cartridges extended to all water matrices
Mass Calibration Verification	Tightened window from .5 amu to .2 amu	No Change	No Change
ICAL	Gave formula for tracking NIS areas, no criteria given	No Change	Removed the no criteria statement, does not specify specific criteria.
	No criteria for calculated concentration.	No specific criteria for concentration, but 70%-130% recommended	No specific criteria for concentration, but 70%-130% recommended
	RSD <20% RSE <20%, must use for linear or quadratic	RSD <20% RSE <20%, must use for linear or quadratic	RSD <20% RSE <20%, must use for linear or quadratic
Extraction	Added info about soils evaporation protocol	No change, new table was never added	New table for final volumes still not added

Alpha internal notes

Parameter	Draft #2	Draft #3	Draft #4
Analysis	Bile Salts added to daily sequence	No Change	No Change
Instrument Sensitivity Check	Instrument sensitivity check no specific criteria	Instrument sensitivity check 70%-130% for all targets	70%130% retained. Alpha will need ti implement.
Calibration Verification	The recovery of native and isotopically labeled compounds for the CVs must be within 70 - 130%.	Targets only must be 70%-130%	The recovery of target analyte and EIS compound for the CVs must be within 70 - 130%
Table 5	Based off single laboratory validation	Updated limits to include MLV wastewater data	Updated for all aqueous matrices. No limits are tighter than draft 3. New draft 4 table 6 has updated NIS and EIS recoveries for all aqueous samples. Alpha will need to adopt/adjust working limits to minimum requirements
Table 6	MDL Data from single lab validation study	began adding in pooled data from MLV for wastewater	Now table 7, full pooled data for aqueous matrices

Alpha internal notes

Overview & Summary- *draft* Method 1633 *rev2*

Sample Containers & Sample Handling

100 mLs

8.0 Sample Collection, Preservation, Storage, and Holding Times

8.2 Aqueous samples

8.2.1 Samples that flow freely are collected as grab samples or in refrigerated bottles using automatic sampling equipment. Collect **500 mL** of sample (other than **leachates**) in an HDPE bottle. Do not fill the bottle past the shoulder, to allow room for expansion during frozen storage.

NOTE: *Because the target analytes are known to bind to the interior surface of the sample container, the entire aqueous sample that is collected must be prepared and analyzed and subsampling avoided whenever possible. Therefore, if a sample volume smaller than 500 mL…*

8.3 Solids

8.3.1 Collect samples as grab samples using wide-mouth jars and fill no more than ¾ full

8.3.2 Maintain solid samples protected from light at 0 - 6 ºC from the time of collection until receipt at the laboratory. Once received by the laboratory, **the samples may be stored at ≤ -20 ºC or at 0 - 6 ºC, until sample preparation.** However, the **allowable holding time for samples depends on the storage temperature,** as described in Section 8.5.

Overview & Summary- *draft* Method 1633 *rev2*

8.3 Solid (soil, sediment, biosolids), 8.4 Tissue

8.3.1 Collect samples as grab samples using wide-mouth jars and fill no more than ¾ full

8.3.2 Maintain solid samples protected from light at 0 - 6 ºC from the time of collection until receipt at the laboratory. Once received by the laboratory, **the samples may be stored at ≤ -20 ºC or at 0 - 6 ºC, until sample preparation.** However, the **allowable holding time for samples depends on the storage temperature,** as described in Section 8.5.

8.4 Fish and other tissue samples

Field sampling plans and protocols **should explicitly state** the samples to be collected and if any processing will be conducted in the field

8.4.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.4.2 If **whole fish** are collected, **wrap the fish in aluminum foil or food-grade polyethylene tubing**, and **maintain at 0 - 6 ºC from the time of collection until receipt at the laboratory, to a maximum time of 24 hours**. If a longer transport time is necessary, freeze the sample before shipping. **Ideally,** fish should be frozen upon collection and shipped to the laboratory on dry ice.

Overview & Summary- *draft* Method 1633
Sample Extraction

- Aqueous samples
  - spiked with isotopically labeled standards, extracted using weak anion exchange (WAX) SPE cartridges with clean up using loose graphitized carbon black (GCB) before analysis.
  - 500 mL Aq sample volume ✓

> **7.1.17** Carbon – EnviCarb® 1-M-USP or equivalent, verified by lot number before use, store at room temperature. Loose carbon allows for better adsorption of interferent organics.
>
> ***Note:*** *The single-laboratory validation laboratory achieved better performance with loose carbon than carbon cartridges. Loose carbon will be used for the multi-laboratory validation to set statistically based method criteria. Once the method is multi-laboratory validated, laboratories will have the flexibility to use carbon cartridges, as long as all method QC criteria are met.*

- Soil samples
  - Spiked w/isotopically labeled standards, sequentially extracted 3 times with slightly basic methanol
    - 60 minutes total, first 2 extractions using shaker table
    - GCB & WAX SPE clean up
  - % solids determination prior to extraction ✓
    - Impact on TAT?

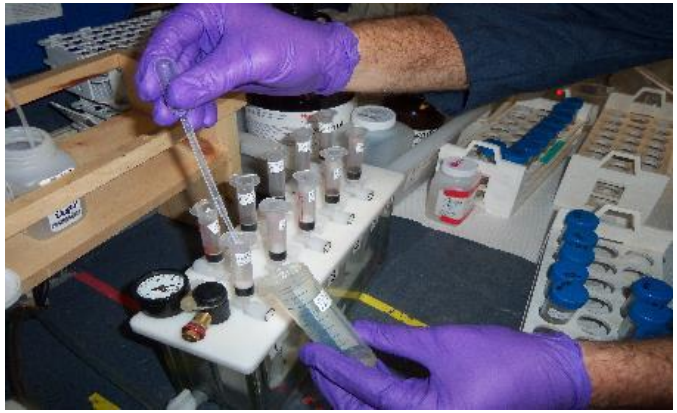

GCB form loose clean-up

AQ Sample Processing, Particulates

- Method 1633 *rev 4*
  - Standard procedure applicable to samples with up to 50 mg suspended solids
    - No filtering
    - Prepare entire sample
    - Homogenize invert 3-4 times
    - Spike w/ EIS
  - *AQ samples w/ >50 mg SS?*
- Appendices A & B
  - Screening & sub sampling
- Particulates will impact SPE performance
  - Wastewater, "silty" ground water, etc.
- How are they addressed ?
  - Additional sample prep required
    - Filtering??
    - Centrifuging?
      - How are the solids accounted for?
- Isotope dilution approach
  - Samples pre-spiked with extraction internal standards

Biosolids / Residuals Sample Extraction

- Challenging…
- Samples pre-spiked with extraction internal standards
  - Homogenize
  - Serial extraction
  - Extract clean up
  - Extract concentration



Overview & Summary- *draft* Method 1633
Instrumental Analysis

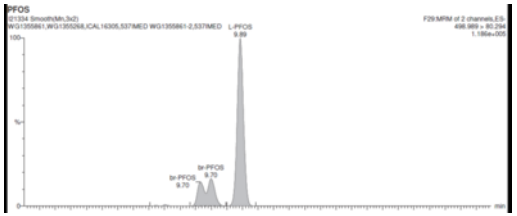
- LC-MS/MS in multiple reaction monitoring mode (MRM)
  - Individual PFAS analytes identified via LC retention time and identification of the quantification & confirmation ions, where applicable
  - Minimum 6-point calibration
  - Method procedure calibrates and quantifies 40 PFAS target analytes, using isotopically labeled compounds prior to extraction by either:

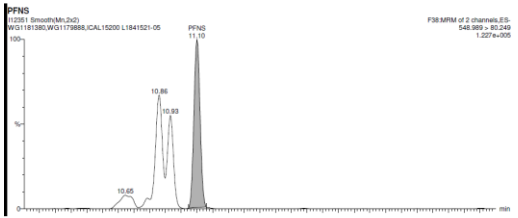
"Section 10.3"

- True isotope dilution quantification (ID), whereby the response of the target compound is compared to the response of its isotopically labeled analog. Twenty-four target compounds are quantified in this way.
- Extracted internal standard quantification (EIS), whereby the response of the target compound is compared to the response of the isotopically labeled analog of another compound with chemical and retention time similarities. Sixteen target compounds are quantified in this way.

Overview & Summary- *draft* Method 1633

Instrumental Analysis – Linear & Branched Isomers





QUANTITATIVE STANDARDS containing a mixture of branched and linear isomers must be used if they are commercially available. Only **4** were/are available **PFOS, PFHxS, NMeFOSAA, and NEtFOSAA.**

QUALITATIVE STANDARDS that contain mixtures of the branched and linear isomers of the method analytes and that are used for comparison against suspected branched isomer peaks in field samples.

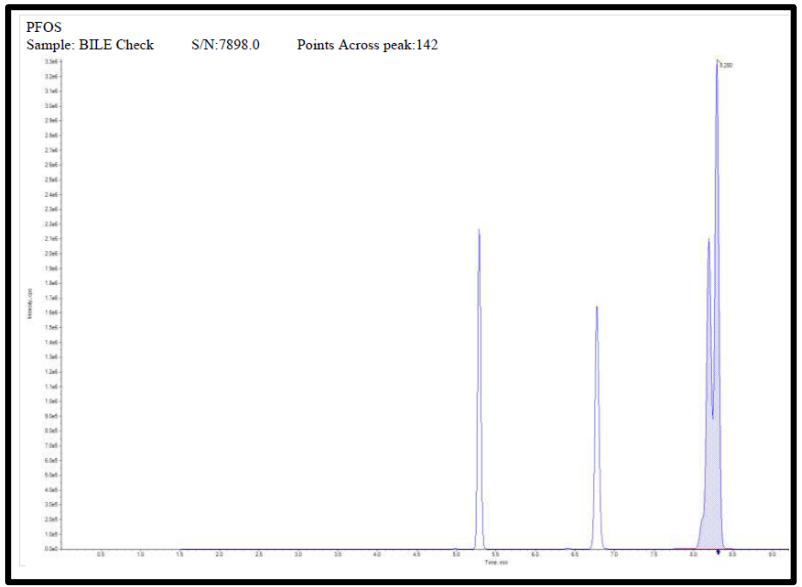
PFOA qualitative standard previously available

- Method 1633 **adds qualitative branched isomer standards for 6 additional PFAS** *(note: linear/branched not reported separately)* **PFNA, PFOSA, NMeFOSA, NEtFOSA, NEtFOSE, and NMeFOSE** **11 / 40 PFAS can be reported as the total of Linear & Branched**

Overview & Summary- *draft* Method 1633

Instrumental Analysis - Bile Salt Interference Check

- Bile salt interference check(s) added to Draft Method 1633
  - **Potential PFOS interferent** in tissue samples primarily



taurodeoxycholic acid (TDCA)

Acetonitrile mobile phase

10.2.2.5 When establishing the chromatographic conditions, it is important to consider the potential interference of bile salts during analyses of tissue samples. Inject the bile salt interference check standard containing TDCA (see Section 7.5 if the mobile phase is not acetonitrile) during the retention time calibration process and adjust the conditions to ensure that TDCA (or TCDCA and TUDCA) does not coelute with any of the target analytes, EIS, or NIS standards. Analytical conditions must be set to allow a separation of at least 1 minute between the bile salts and the retention time window of PFOS

Must also include if acetonitrile is not the mobile phase and tissues are being analyzed

taurochenodeoxycholic acid (TCDCA)
tauroursodeoxycholic acid (TUDCA)

Overview & Summary- *draft* Method 1633

Holding Times

8.5 Holding times

8.5.1 Aqueous samples (including leachates) should be analyzed as soon as possible; however, samples may be held in the laboratory for up to 90 days from collection, when stored at ≤ -20 ºC and protected from the light. When stored at 0 - 6 ºC and protected from the light, aqueous samples may be held for up to 28 days, with the caveat that issues were observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days. These issues are more likely to elevate the observed concentrations of other PFAS compounds via the transformation of these precursors if they are present in the sample.

8.5.2 Solid samples (soils and sediments) and tissue samples may be held for up to 90 days, if stored by the laboratory in the dark at either 0 - 6 ºC or ≤ -20 ºC, with the caveat that samples may need to be extracted as soon as possible if NFDHA is an important analyte.

8.5.3 Biosolids samples may be held for up to 90 days, if stored by the laboratory in the dark at 0 - 6 ºC or at -20 ºC. Because microbiological activity in biosolids samples at 0 - 6 ºC may lead to production of gases which may cause the sample to be expelled from the container when it is opened, as well as producing noxious odors, EPA recommends that samples be frozen if they need to be stored for more than a few days before extraction.

8.5.4 Store sample extracts in the dark at less than 0 - 4 ºC until analyzed. If stored in the dark at less than 0 - 4 ºC, sample extracts may be stored for up to 90 days, with the caveat that issues were observed for some ether sulfonates after 28 days. These issues may elevate the observed concentrations of the ether sulfonates in the extract over time. Samples may need to be extracted as soon as possible if NFDHA is an important analyte.

Holding Time Comparison

Sample Media	537.1 sample	537.1 extract	533 sample	533 extract	8327 sample	8327 extract	1633 draft sample	1633 draft extract
drinking water	14 days	28 days	28 days	28 days	X	X	X	X
aqueous	X	X	X	X	14 days*	30 days*	0-6C 28 days** <= -20C 90 days DARK	DARK 0-4C 90 days *****
soils, sediments	X	X	X	X	X	X	0-6C 90 days*** <= -20C 90 days***DARK	DARK 0-4C 90 days *****
biosolids	X	X	X	X	X	X	0-6C 90 days**** **<= -20C 90days****DARK**	DARK 0-4C 90 days *****
tissue	X	X	X	X	X	X	Once received by the laboratory, the samples must be **maintained protected from light** at ≤ -20 °C until prepared. Store unused samples in HDPE containers or wrapped in aluminum foil at ≤ -20 °C.	0-4C 90 days ***** **maintained protected from the light**

* Formal holding times have not yet been established for these analytes in various matrices.

** With the caveat that issues were observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days. These issues are more likely to elevate the observed concentrations of other PFAS compounds via the transformation of these precursors if they are present in the sample.

*** with the caveat that samples may need to be extracted as soon as possible if NFDHA is an important analyte.

**** EPA recommends that samples be frozen if they need to be stored for more than a few days before extraction.

***** with the caveat that issues were observed for some ether sulfonates after 28 days. These issues may elevate the observed concentrations of the ether sulfonates in the extract over time.

Method 1633 Comparability with “User Defined” Method?

- Disclaimer: new method, not a lot of commercial samples run yet
  - Little comparison data available, there are potential procedural differences
    - *That said, routine, relatively clean matrices / “usual suspect” PFAS **should** be comparable*
- Obvious questions
  - Target compound lists, Reporting limits
- More complex matrices?
  - Comparability concerns w/draft 1633 vs. lab user defined methods possible
    - However, the specific inconsistencies will differ depending on the lab’s user defined SOP and the sample being analyzed
      - Interferences due to matrix, AQ particulates, non-target PFAS and linear to branched isomer pattern, etc. could impact each method differently

United States Environmental Protection Agency

Office of Water

www.epa.gov April 2022

Draft Method 1621

Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)

Method is 60% thru multi-lab validation study

DRAFT Method 1621 – Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)

1.0 Scope and Application

1.1 Method 1621 is for use in the Clean Water Act (CWA) as a screening method to estimate the concentration of adsorbable organic fluorine (AOF) in aqueous matrices by combustion ion chromatography (CIC).

1.2 The method measures organofluorine compounds from per- and polyfluoroalkyl substances (PFAS) and non-PFAS fluorinated compounds such as pesticides and pharmaceuticals that can be retained on at least 80 mg of granular activated carbon (GAC). The result is reported as the concentration of fluoride (F^-) in the sample.

1.3 Short-chain (less than 4 carbons) organofluorine compounds are poorly retained on GAC while long-chain (more than 8 carbons) hydrophobic organofluorine compounds readily adsorb to surfaces. These issues can cause low recoveries for these types of fluorinated compounds.

1.5 Relative to the Clean Water Act and the methods approved for compliance monitoring at 40 CFR Part 136, AOF is a "method-defined parameter" (MDP). A MDP is a parameter defined solely by the method used to determine the analyte. In the case of AOF, Draft Method 1621 estimates an aggregate concentration of any organofluorine compounds in the sample that are retained on the sorbent. Therefore, EPA has limited the extent to which this method may be modified without prior EPA review. At this time, the analyst may not use sorbents other than granular activated carbon, amounts of granular activated carbon less than 80 mg per sample, or sample containers made from different materials. EPA may include additional restrictions following completion of the multi-laboratory validation study.

1.7 For the reasons discussed in Sections 1.2 to 1.6, EPA has classified this procedure as a screening method that may be used to estimate the aggregate contributions of the organofluorine compounds present in the sample. As such, data users are advised that the numerical results generated by this method are not expected to be as accurate or precise as those from targeted methods for PFAS. In addition, given the large number of potential PFAS and other organofluorine compounds that may be present in environmental samples, EPA has adjusted some of the quality control and method performance testing approaches employed in this procedure to those more suited for a screening method.

2.0 Summary of Method

2.1 Environmental aqueous samples are prepared and adsorbed using method-specific procedures. A 100-mL sample aliquot is passed through two GAC columns, each containing 40 mg of carbon.

2.2 The GAC columns are rinsed with sodium nitrate to remove inorganic fluoride, combusted at least 1000 °C in an oxygen or oxygen/argon stream, and the gaseous hydrogen fluoride is absorbed into reagent water.

2.3 The fluoride is separated by ion chromatography (IC) and identified by comparing sample fluoride retention time to retention times for calibration standards acquired under identical IC conditions and by using the external standard technique.

Wrap up

- Method 1633
  - Aq samples w/particulates
    - Still a “grey area”
  - Bile salt interference check for tissues
  - Branched isomers standards for 6 additional PFAS compounds
  - Holding time differences
- Method 1621 - AOF
  - Screening and draft method
  - Proxy for “total PFAS”
- **Obvious benefit from having a final, standardized method for all environmental media**


Questions?