



PFAS Analytical Methods

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Today's Speaker



Janice Willey
NAVSEA

Objectives



- **Insight into currently available PFAS analytical methods**
- **An understanding of how these methods relate to current policy and guidance**
- **Provide information on future methods and their implication on future policy and guidance**

EPA Drinking Water Methods



- **EPA Method 537.1**

- Applicable to drinking water sources only
- Includes 18 PFAS, four not included in EPA 533 (NEtFOSAA, NMeFOSAA, PFTA, PFTrDA)
- 20 DoD Environmental Laboratory Accreditation Program (ELAP) laboratories are accredited for “EPA 537.1”
- Current DoD policy requires use of this method for DW

EPA Drinking Water Methods



- **EPA Method 533**

- Applicable to drinking water sources only
- Includes 25 PFAS, 14 overlap with EPA 537.1, 11 are unique to EPA 533 (4:2 FTS, 6:2 FTS, 8:2 FTS, NFDHA, PFBA, PFEESA, PFHpS, PFMBA, PFMPA, PFPeA, PFPeS)
- 11 DoD ELAP laboratories are accredited for “EPA 533”
- Currently no DoD policy requires use of this method, however...

UCMR5



- **Effective 01/29/22**

- **Sample collection from January 2023 through December 31, 2026**
- **Analyses required:**
 - Lithium by EPA 200.7, MRL of 9 ppb
 - NMeFOSAA, NEtFOSAA, PFTA, & PFTTrDA by EPA 537.1, MRLs range from 5 to 8 ppt
 - All 25 PFAS listed in EPA 533 by EPA 533, MRLs range from 2 to 20
- **Currently 24 laboratories are EPA approved to perform all three analyses, 11 additional laboratories are accredited for 1 or 2 of these analyses**

<https://www.epa.gov/dwucmr/laboratory-approval-program-unregulated-contaminant-monitoring-rule-ucmr-5>

UCMR5 – PFAS Minimum Reporting Limits (MRLs)



EPA 533 Analytes	MRL	EPA 533 Analytes	MRL
11Cl-PF3OUdS	5 ppt	PFDA	3 ppt
8:2FTS	5 ppt	PFDoA	3 ppt
4:2FTS	3 ppt	PFHpS	3 ppt
6:2FTS	5 ppt	PFHpA	3 ppt
ADONA	3 ppt	PFHxS	3 ppt
9Cl-PF3ONS	2 ppt	PFHxA	3 ppt
HFPO-DA	5 ppt	PFNA	4 ppt
NFDHA	20 ppt	PFOS	4 ppt
PFEESA	3 ppt	PFOA	4 ppt
PFMPA	4 ppt	PFPeS	4 ppt
PFMBA	3 ppt	PFPeA	3 ppt
PFBS	3 ppt	PFUnA	2 ppt
PFBA	5 ppt		

EPA 537.1 Analytes	MRL
NEtFOSAA	5 ppt
NMeFOSAA	6 ppt
PFTA	8 ppt
PFTrDA	7 ppt

SW-846 PFAS Methods



- **SW-846 Methods 3512 & 8327**

- Applicable to non-potable aqueous samples only
- Includes 24 PFAS, does not include all analytes in EPA Methods 537.1 or 533
- Direct injection, external calibration quantitation
- Considered to be an screening method by DoD (DoD Memorandum dtd 22 November 2019 & DoD Environmental Data Quality Workgroup (EDQW) Statement on EPA Method 8327, <https://denix.osd.mil/edqw>)

No DoD ELAP laboratory is accredited for this method & will never be since it is a SCREENING method

EPA Draft Method 1621



• Basics

- Published in April 2022 (<https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas>)
- Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)
- Single-laboratory validated for organofluorines in wastewater
- Estimates an aggregate concentration of organofluorine content, which includes PFAS and non-PFAS fluorinated compounds (e.g. pesticides & pharmaceuticals)
- Screening due to the fact it does not quantify all organofluorines and is limited by the presence of significant interferences
- NOT a PFAS-only determination

EPA Air Method



- **Draft Other Test Method 45 (OTM-45)**

- Applicable to emissions sampling from stationary sources, NOT ambient air sampling
- Sample collection, preparation, & analysis of 50 PFAS (semi-volatile and particle-bound)
- Utilizes filters, impingers, & sorbent media (XAD-2) for sample collection, resulting in four discreet sample extracts per sampling location
- Isotope dilution/extracted internal standard quantitation
- Non-targeted analysis (NTA) can be performed on these samples, however, the analytical procedure for NTA is not included in this method
- A component of the evaluation of thermal treatment technologies for destruction of PFAS-laden materials

Requirements for Matrices Other than DW



- **Before December 31, 2021**

- DoD Memorandum dtd 22 November 2019 & the NAVFAC PFAS Guidance Document required use of methods that were compliant with DoD/DOE Quality Systems Manual (QSM), Table B-15

- **Requirements for accreditation found in:**

- DoD/DOE QSM (Tables B-15, C-44, & C-45) ONLY, no other document required

DoD/DOE QSM, Table B-15 is NOT a method; only a table of quality control requirements.

It was always intended to be a temporary solution until an appropriate method was published.

Requirements for Matrices Other than DW



- **After December 31, 2021**
 - **DoD Memorandum dtd 28 October 2021**
 - Requires all new contracts and task orders after December 31, 2021 to use EPA Draft Method 1633 for analysis of matrices other than drinking water using a DoD ELAP laboratory accredited for this method
 - Encourages existing projects to require EPA Draft Method 1633 to be used
- **Requirements for accreditation found in:**
 - EPA Draft Method 1633
 - EPA Errata Sheets
 - DoD/DOE QSM, Version 5.4, Table B-24
- **3 DoD ELAP laboratory is accredited for “Draft EPA Method 1633”**

Table B-24



• Table B-24 Goals

- Meet DoD data quality needs
- Maintain consistency with EPA 1633
- Include requirements in addition to those in EPA 1633 when more stringent requirements are needed
- Provide temporary QC acceptance criteria until the final method is published

****ALL OF THE REQUIREMENTS CONTAINED IN EPA DRAFT METHOD 1633 MUST BE MET. This table contains additional requirements that must be met. Where the name for the QC sample listed in this table differs from EPA Draft Method 1633 terminology, the corresponding EPA Draft Method 1633 terminology is provided in the Comments column.****

EPA Draft Method 1633



• Basics

- Published in September 2021 (<https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas>)
- Applicable to groundwater, surface water, wastewater, landfill leachates, soil, sediment, biosolids, & tissue
- 40 PFAS, includes all PFAS applicable to EPA 537.1, 533, & SW-846 Method 8327 and 8 additional analytes:
 - NEtFOSA
 - NMeFOSA
 - NEtFOSE
 - NMeFOSE
 - 3:3FTCA
 - 5:3FTCA
 - 7:3FTCA
 - PFDoS

EPA Methods 537.1, 533, & 1633 Analyte List Comparison



Analyte	EPA 533	EPA 537.1	EPA 1633
11Cl-PF3OUdS	x	x	x
9Cl-PF3ONS	x	x	x
ADONA	x	x	x
HFPO-DA	x	x	x
PFBS	x	x	x
PFDA	x	x	x
PFDaA	x	x	x
PFHpA	x	x	x
PFHxA	x	x	x
PFHxS	x	x	x
PFNA	x	x	x
PFOA	x	x	x
PFOS	x	x	x
PFUnA	x	x	x
4:2FTS	x		x
6:2FTS	x		x
8:2FTS	x		x
NFDHA	x		x
PFBA	x		x
PFEESA	x		x
PFHpS	x		x
PFMBA	x		x
PFMPA	x		x
PFPeA	x		x
PFPeS	x		x
NEtFOSAA		x	x
NMeFOSAA		x	x
PFTeDA or PFTA		x	x
PFTrDA		x	x
NEtFOSA			x
NMeFOSA			x
NEtFOSE			x
NMeFOSE			x
3:3FTCA			x
5:3FTCA			x
7:3FTCA			x
PFOSA			x
PFDoS			x
PFDS			x
PFNS			x

EPA Draft Method 1633



• Basics

- **Media specific sample preparation procedures (aqueous, solid, tissue)**
- **Analysis by LC-MS/MS method using isotope dilution/extracted internal standard quantitation**
- **Validated by the Strategic Environmental Research and Development Program (SERDP)**
 - Single-laboratory study completed, report published
 - Multi-laboratory validation underway

Impact of Transition to EPA Draft Method 1633



• Sample Collection

- **Specific requirements for in-field compositing equipment**
 - Only HDPE tubing **must** be used in compositing equipment, except for a minimum length of silicon rubber tubing in the pump. Integrated flow meter is used to collect proportional composite samples (Section 6.1.2)
- **Size, type, & number of sample bottles is specified**
- **Storage & Shipping requirements are provided**
- **Holding times**
 - Based on results of holding time study (except for tissue)
 - Dependent on storage temperature and analytes of interest
 - Method provides the laboratory with options
 - Project must specify which option is required for their project; NOT the laboratory

EPA Draft Method 1633: Sample Collection



Matrices	Type of Container	Sample Size per Sample	Sample Shipping
Aqueous (GW, WW, SW)	One 500 mL HDPE bottle with linerless HDPE or PP caps & one lesser volume (125-250 mL) HDPE bottle with linerless HDPE or PP caps, filled to the shoulder of bottle	500 mL for sample analysis & a minimum of 20 mL needed for screening	<ul style="list-style-type: none"> - Protect from light at 0 - 6°C from time of collection until shipped. - Maintain 0 - 6°C during shipping - Receive in lab within 48 hrs of collection
Aqueous (Landfill Leachate)	Two 125 mL HDPE bottle with linerless HDPE or PP caps, filled to the shoulder of bottle	100 mL for sample analysis & 100 mL needed for screening	
Solid (soil, sediment)	wide-mouth high density polyethylene (HDPE) jar or bottle with linerless HDPE or polypropylene caps, fill no more than 3/4 full	- 5.0 grams dry weight	<ul style="list-style-type: none"> - Protect from light at 0 - 6°C from time of collection until shipped. - Maintain 0 - 6°C during shipping
Biosolids		- 0.5 grams dry weight	
Tissue	One 500 mL HDPE bottle with linerless HDPE or PP caps, if whole fish, wrap in aluminum foil or food-grade polyethylene warp	- 2.0 grams homogenized	<ul style="list-style-type: none"> - Maintain 0 - 6°C from time of collection until received by lab if received within 24 hrs - If longer transport is needed, recommend freeze prior to shipping and shipment on dry ice, if possible

EPA Draft Method 1633: Laboratory Holding Times



Matrices	Stored at 0 - 6 °C, protected from light		Stored at ≤ -20 °C, protected from light	
	Holding Time	Exceptions	Holding Time	Exceptions
Samples				
Aqueous	28 days	Precursor degradation after 7 days	90 days	None
Solid	90 days	NFDHA - analyze as soon as possible	90 days	NFDHA - analyze as soon as possible
Biosolid	90 days		90 days	None
Extracts	Stored at 0 - 4 °C, Protected from light			
Aqueous	90 days	28 days for ether sulfonates	NA	None
Solid	90 days	28 days for NFDHA	NA	None
Biosolid	90 days		NA	None

Impact of Transition to EPA Draft Method 1633



- **Sample Preparation:**

- **Aqueous samples must be screened using a different container than the one used for preparation and analysis**
- **Detailed procedures for each matrix type**
- **All samples to undergo SPE and carbon cleanup**
 - Aqueous samples – whole sample is extracted via SPE & extracts undergo carbon clean-up
 - Solid samples (soil, sediment, biosolids, tissue) – undergo extracted via liquid extraction & extracts are clean-up up via SPE & carbon clean-up
 - AFFF and other high concentration samples – an aliquot of sample is diluted & that dilution undergoes the same processes as all other aqueous samples (extracted via SPE & extracts undergo carbon clean-up)
 - Table B-24 requires the Section 11.2.6 of DoD AFFF01 to be followed

Impact of Transition to EPA Draft Method 1633



- **Sample Preparation:**

- **Batch QC Samples include:**

- Method Blank (MB)
 - Laboratory Control Sample (LCS),
 - Low-Level LCS (LLCS), spiked at two times the LOQ
 - Matrix Spike & Matrix Spike Duplicate (Table B-24)
 - Matrix Duplicate (MD), applicable to AFFF samples only (Table B-24)

- **24 Extracted internal standards (EISs) are spiked into each sample prior to extraction (whole water samples spiked in sample container)**

- **7 Non-extracted internal standards (NISs) are spiked into each extract prior to analysis**

Impact of Transition to EPA Draft Method 1633



- **Sample Analysis:**

- Requires the analysis of a bile salts standards daily, regardless of matrix type of samples (Table B-24)
- Requires the analysis of Qualitative Standards daily
- Requires ion masses identified in method to be used for analytes that have commercially available isomeric mixtures of the analyte (Table B-24)
- Requires daily analysis of an Instrument Sensitivity Check (ISC) and must recover within 70-130% of true value for all analytes (recovery criteria from Table B-24)
- Calibration criteria is different
- Initial Calibration Verification (ICV) is required after ICAL (Table B-24)

Impact of Transition to EPA Draft Method 1633



- **Sample Analysis:**

- **MB acceptance criteria (Table B-24)**
- **LCS and LLLCS acceptance criteria (Table B-24)**
 - Target analytes – in-house recovery limits with lower limit not to be < 40%
- **MS/MSD acceptance criteria (Table B-24)**
 - Target analytes – in-house recovery limits with lower limit not to be < 40%, and MS/MSD RPD must be $\leq 30\%$
- **Sample/MD acceptance criteria (Table B-24)**
 - Target analytes – RPD must be $\leq 30\%$

Impact of Transition to EPA Draft Method 1633



- **Sample Analysis:**
 - **Ion Ratio acceptance criteria**
 - Ion ratio defined as total quantitation ion: total confirmation ion
 - Target analytes with concentrations \geq LOQ – ion ratio must fall within \pm 50% of ratio observed in mid-point ICAL standard
 - Target analytes with concentrations $>$ MDL but $<$ LOQ – ion ratio must fall within \pm 50% of ratio observed in initial daily CCV (Table B-24)
 - **EIS acceptance criteria**
 - In-house limits with lower limit not to be $<$ 20% (Table B-24)
 - **NIS acceptance criteria**
 - NIS areas must be $>$ 30% of the average area of the calibration standards (Table B-24)

Fire-Fighting Foam Concentrate Methods



- **DoD AFFF01, Rev. 1.0:**
 - **Applicable to AFFF concentrates for demonstration of compliance to MIL-PRF-24385**
 - **PFOA & PFOS, LOQ 25 ppb or less**
 - **Similar method to EPA Draft Method 1633**
 - Includes requirements designed to ensure homogeneity of dilution prior to extraction
 - Requires samples to be prepared and analyzed in duplicate
 - Requires an LCS Duplicate (LCSD) instead of an MS/MSD
 - Isotope dilution quantitation
 - **Available at <https://denix.osd.mil/edqw>**

Fire-Fighting Foam Concentrate Methods



- **DoD F3-001:**
 - Applicable to fluorine-free foam concentrates for demonstration of compliance to future Military Specification for fluorine-free foams (F3)
 - Total Fluorine, LOQ 0.5 ppb total fluorine or less (equates to 1 ppb or less of total PFAS)
 - Sample preparation via hydrothermal alkaline treatment (HALT), activated alumina extraction
 - Analysis via Ion Chromatography
 - Currently undergoing single-laboratory validation (SLV)
 - Will be published as a single-laboratory validated method
 - Multi-laboratory validation will follow SLV

Future Methods



- **Leachate Methods:**
 - LEAF Methods are currently being evaluated & optimized (ESTCP Project)
- **Non-target analysis Methods**
- **TOF Methods for a variety of matrices**



Thank you!

Questions and Answers



Points of Contact

- **Janice Willey**
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Wrap Up



Next OER2:

Use of an Abbreviated Accident Prevention Plan and Lessons Learned (August 3, 2022)

Thank you for participating!