



PFAS Analytical Methods

Update

DOE ASP Annual Training Workshop Series

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EPA Published Methods Update

Drinking Water

- ***EPA 537.1, Version 2.0, March 2020***
 - *18 PFAS, four not included in EPA 533 (NEtFOSAA, NMeFOSAA, PFTA, PFTrDA)*
 - *Version 2.0 published March 2020*
 - *Version 2.0 changed requirements for field reagent blank*
 - *Applicable to drinking water only*
 - *Solid-phase extraction (SPE) & Internal Standard Quantification*
 - *Current DoD policy requires its use for drinking water samples*
 - *DoD ELAP identification in DENIX database is "EPA 537.1"*
 - *UCMR5 proposal states NEtFOSAA, NMeFOSAA, PFTA, & PFTrDA analysis by EPA 537.1*



EPA Published Methods Update

Drinking Water

- ***EPA 533, December 2019***
 - *Published December 2019*
 - *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)*
 - *Applicable to drinking water only*
 - *SPE & Isotope Dilution/Extracted Internal Standard Quantification*
 - *DoD ELAP identification in DENIX database is “EPA 533”*
 - *UCMR5 proposal states all 25 PFAS included in EPA 533 method analyte list analyzed by EPA 533*



EPA Published Methods Update



Air:

- ***DRAFT Other Test Method (OTM) 45, June 2019***
 - *Sample collect, preparation, & analysis of 50 PFAS (semi-volatile & particle-bound) in emissions from stationary sources*
 - *Utilizes filters, impingers, & sorbent media (XAD-2) for sample collection, resulting in four discreet sample extract fractions*
 - *Analysis by LC-MS/MS & 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*



EPA Published Methods Update

Non-potable Water:

- ***EPA SW-846 Methods 3512 & 8327, July 2021***
 - *24 PFAS (does not include all PFAS in EPA 537.1 or EPA 533)*
 - *Solvent Extraction & External Calibration Quantification*
 - *Multi-laboratory study data from 8 laboratories analyzing a single sample for GW (DW supply well), SW, & WW effluent. Each extracted 5 times each not spiked, spiked at 60 ppt, and spiked at 200 ppt.*
 - *6:2 FTS did not meet criteria for acceptable performance*
 - *PFUnDA, PFDoDA, PFTrDA, PFTeDA, N-MeFOSAA, & N-EtFOSAA showed a potential for loss either during standard preparation or sample preparation*



EPA Published Methods Update

Non-potable Water:

- ***EPA SW-846 Methods 3512 & 8327, July 2021***
 - *DoD Memorandum 22 November 2019 prohibits use of this method as it requires testing of media other than DW to comply with DoD QSM Table B-15 requirements*
 - *For DoD EDQW statement regarding this method follow the link on the DENIX EDQW Webpage “DoD EDQW Statement on EPA Method 8327” at: <https://www.denix.osd.mil/edqw/home/>*



NAVSEA Published Method



- **Draft DoD AFFF01, Rev. 1.0**

- *PFOA & PFOS in Class B AFFF concentrates.*
- *Applicable to testing performed to demonstrate compliance with the upcoming revision to the military performance specification for Fire Extinguishing Agent, Aqueous Film-Forming Foam (AFFF) Liquid Concentrate, for Fresh and Sea Water (MIL-PRF-24385)*
- *SPE & Isotope Dilution Quantification*
- *Applicable media includes AFFF and AR-AFFF concentrates*
- *Achieves lower LOQs of <25 ppb PFOA & PFOS*
- *More prescriptive than methods applicable to environmental media due to the untended use of the data*
- *Comments on method requested by October 31, 2021*
- *Draft method and comment form at: <https://denix.osd.mil/edqw/>*



Future Draft EPA 1633 Method

- **Draft EPA 1633**

- 40 PFAS (includes all PFAS applicable to EPA 537.1, 533, & SW-846 Method 8327 and 8 additional analytes not covered by these methods)
- Applicable to groundwater, surface water, wastewater, landfill leachates, soil, sediment, biosolids, & tissue
- SPE & Isotope Dilution/Extracted Internal Standard Quantification
- Validated by the Strategic Environmental Research and Development Program (SERDP) in coordination with the EPA OW and EPA OLEM
- Single laboratory study data included analysis of 3 unique samples each for GW, SW, landfill leachate, sediment, biosolids, & tissue and 7 unique samples each for WW & soil. Each extracted 3 times each not spiked, spiked at 2.5x, 5x, and 7.5x LOQ in aqueous samples, & 4x, 6x, and 10x LOQ in solids and tissue



Future Draft EPA 1633 Method



- **Draft EPA 1633**

- Utilizes 24 Extracted Internal Standard (EIS) and 7 Non-extracted Internal Standards (NIS)
- Media specific sample preparation procedures included for aqueous, solid (soil, sediment & biosolids), & tissue
- Utilizes SPE (WAX) and carbon clean-up steps & includes mechanism to address high PFAS concentration samples
- Requires preparation of a LOQ verification QC sample on a batch basis
- Includes analysis of a standard to confirm bile salts would not interfere with the quantification of PFOS, if present
- NO "Dilute and shoot" option for higher concentration samples; all aqueous samples go through extraction via SPE & carbon cleanup



Future Draft EPA 1633 Method

- **Draft EPA 1633**

- *Includes storage, preservation, & holding time requirements based on actual holding time study data!!!*
- *Multi-laboratory validation study is ongoing with participation from 8 DoD ELAP-accredited laboratories and 2 State laboratories*
- *DoD EDQW is revisiting the requirements for PFAS analysis contained in the DoD/DOE QSM, Table B-15 and the DoD PFAS Data Validation Guidelines*



Methods In Development

- **Determination of Total Organic Fluorine (TOF) Content in Fire-fighting Agents**
 - *SERDP-funded and NRL-led*
 - *Method to address the requirement in the NDAA to utilize a “fluorine-free” fire-fighting agent by Oct. 1, 2023 that contains no more than 1 ppb of PFAS*
 - *Steps needed to eliminate/account for inorganic fluorine in sample*
 - *Hydrothermal alkaline treatment of sample to mineralize fluorine*
 - *Fluorine preconcentration step*
 - *Analysis by IC or ISE*



Methods In Development

- **EPA**

- *OW: 1600-Series method for absorbable organic fluorine (TOF by CIC)*
- *ORD: Non-targeted analysis for aqueous, solids, & air*
- *ORD: TOF by CIC air emissions*
- *ORD TOP Assay*



Thank you!

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