Federal Drinking Water Program Update

Environmental Measurement Symposium
August 8, 2024

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Overview

- *PFAS National Primary Drinking Water Regulation (NPDWR)*
- *Drinking Water Analytical Methods Development*
- *Method Approval*
  - *Recent Expedited Method Approval Action - January 2024*
  - *Status of Drinking Water Method Update Rule (MUR)*
- *Unregulated Contaminant Monitoring Rule (UCMR)*

PFAS NPDWR – 40 CFR Part 141, Subpart Z

- Final rule announced April 10, 2024 establishing legally enforceable standards for six PFAS in drinking water:
  - PFOA, PFOS, PFHxS, PFNA, and HFPO-DA with individual Maximum Contaminant Levels (MCLs)
  - PFAS mixtures containing at least two or more of PFHxS, PFNA, HFPO-DA, and PFBS using a Hazard Index MCL to address combined/co-occurring PFAS in drinking water.
- Established health-based, non-enforceable Maximum Contaminant Level Goals (MCLGs) for these PFAS.
- Laboratories must follow approved methods (EPA Methods 533 or 537.1 ver2):
  - Establish minimum reporting levels (MRLs) at or below regulatory practical quantitation limits (PQLs)
  - Meet MRL confirmation acceptance criteria in each analytical batch of samples
  - Pass laboratory reagent blank (LRB) criteria, i.e., nothing qualitatively detected >1/3 MRL.

https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

PFAS NPDWR – 40 CFR Part 141, Subpart Z

Analyte	Trigger Level[1] (mg/L)	PQL[2] (ng/L)	MCL (mg/L)
PFOA	0.0000020 (2.0 ng/L)	4.0	0.0000040 (4.0 ng/L)
PFOS	0.0000020 (2.0 ng/L)	4.0	0.0000040 (4.0 ng/L)
HFPO-DA	0.000005 (5 ng/L)	5.0	0.00001 (10 ng/L)
PFHxS	0.000005 (5 ng/L)	3.0	0.00001 (10 ng/L)
PFNA	0.000005 (5 ng/L)	4.0	0.00001 (10 ng/L)
Hazard Index[3] PFAS (HFPO-DA, PFBS, PFHxS, PFNA)	0.5 (unitless)	N/A	1 (unitless)

[1] Trigger levels used to determine monitoring frequency and to establish "detection" for purposes of consumer confidence reporting (CCR).

[2] The PQL for PFBS is 3.0 ng/L

[3] The Hazard Index is a tool used to evaluate potential health risks from exposure to chemical mixtures.

PFAS NPDWR Laboratory Requirements

- Laboratories must be certified/accredited following the approved methods
- Initial calibration - A minimum of 5 calibration standards, including lowest level at or below the MRL
- Low-level calibration check (Low-level CCC/CCV) – Included in each Analysis Batch
- Mid- and High-level calibration checks (Mid- & High-CCC/CCVs) – Alternate every 10 Field Samples including one at the end of Analysis Batch
- Laboratory Reagent Blank (LRB) – prepared with each Extraction Batch
- Laboratory Fortified Blank (LFB) – prepared with each Extraction Batch, alternating fortification levels and rotating between low, medium, and high concentrations
- Field Samples – No more than 10 between calibration checks, and no more than 20 per analysis batch
- Additional QC Samples (QCS, LFSM/D, FD, FRB) – See method for frequency and passing criteria

PFAS NPDWR Laboratory Requirements

- Quantitation technique
  - Isotope Dilution (Method 533)
  - Internal Standard (Method 537.1, ver. 2.0)
- Linear or Quadratic Calibration Curve forced through zero
- Calibration curves should extend over no more than 2 orders of magnitude
- Linear and branched isomers must be accounted for with all samples
- Field Reagent Blank
  - Ensure target analytes are not introduced into samples during sample collection and handling
  - One FRB for each field sample location
  - FRB analysis only required when associated field sample contains method analytes
  - Failure of FRB invalidates detections of the same target analyte in associated field sample

PFAS Laboratory Initial Demonstration of Capability

QC Sample	EPA Method 533	EPA Method 537.1, v. 2.0
Demonstration of Low System Background	<1/3 MRL	<1/3 MRL
Demonstration of Precision	RSD <20%	RSD <20%
Demonstration of Accuracy	70-130% Recovery	70-130% Recovery
MRL Confirmation	Upper PIR ≤150% Lower PIR ≥50%	Upper PIR ≤150% Lower PIR ≥50%
Quality Control Standard (QCS)	70-130% of the true value	70-130% of the true value

- The IDC must be successfully performed prior to analyzing field samples. The IDC must be repeated if changes are made to analytical parameters not previously validated during the IDC.

PFAS Laboratory Ongoing Demonstration of Capability For Blanks

QC Sample	EPA Method 533	EPA Method 537.1, v. 2.0
Laboratory Reagent Blank (LRB)	<1/3 MRL	<1/3 MRL
Field Reagent Blank (FRB)	≤1/3 MRL when FS ≥MRL	≤1/3 MRL when FS ≥MRL

- An LRB is included in each Extraction Batch to determine if the method analytes or other interferences are introduced from the laboratory environment, the reagents, glassware, or extraction apparatus.
- The purpose of the FRB is to determine if method analytes or other interferences are introduced into the sample from shipping, storage, and the field environment.
- The FRB is only required if method analytes are measured in the associated field sample.
- Measurement between 1/3 MRL and MRL is expected to be qualitative, demonstrating no trace PFAS is being observed in the LRB or FRB.

PFAS Laboratory Ongoing Demonstration of Capability
PFAS Recovery Criteria

QC Sample	EPA Method 533	EPA Method 537.1, v. 2.0
Continuing Calibration Check (CCC)	Low CCC, 50-150% Recovery Mid/High CCC, 70-130% Recovery	Low CCC, 50-150% Recovery Mid/High CCC, 70-130% Recovery
Laboratory Fortified Blank (LFB)	When ≤2X MRL, 50-150% Recovery When >2X MRL, 70-130% Recovery	When ≤2X MRL, 50-150% Recovery When >2X MRL, 70-130% Recovery
Laboratory Fortified Sample Matrix/Duplicate (LFSM/D)	When ≤2X MRL, 50-150% Recovery When >2X MRL, 70-130% Recovery	When ≤2X MRL, 50-150% Recovery When >2X MRL, 70-130% Recovery
Quality Control Standard (QCS)	70-130% of the true value	70-130% of the true value

- CCC verifies the accuracy of the existing calibration.
- LFB verifies method performance in the absence of sample matrix.
- LSFM/D determines whether the sample matrix contributes bias to the analytical results.
- QCS verifies the integrity of the primary calibration standards.

PFAS Laboratory Ongoing QC Acceptance Criteria For Isotopically Labeled Stds

QC Sample	EPA Method 533	EPA Method 537.1, v. 2.0
Internal Standard (IS)	X	50-150% recovery and 70-140% from the most recent CCC.
Surrogate Standard (SUR)	X	70-130% recovery
Isotope Dilution Analogue (IDA)	50-200% recovery and 70-130% recovery in CCCs	X
Isotope Performance Standard (IPS)	50-150% recovery	X

- IS measures the relative response of other method analytes and surrogates (post-extraction/quantitation).
- SUR monitors method performance (extraction efficiency) with each sample (pre-extraction).
- IDA measures the relative response of the method analytes (pre-extraction/quantitation).
- IPS measures the relative response of the isotopically labelled analogues (post-extraction).
- The methods give some flexibility on the selection and use of isotopically labeled standards

PFAS NPDWR – 40 CFR Part 141, Subpart Z

Performance Evaluation (PE) Passing Criteria

Analyte	Acceptance Limits (% of true value)
PFOA	70-130%
PFOS	70-130%
PFNA	70-130%
PFHxS	70-130%
PFBS	70-130%
HFPO-DA	70-130%

Note: The “80% Rule” for passing (e.g., passing 16 of 20 regulated VOCs), IS NOT applicable.

PFAS Method General Flexibility

YES	NO
LC columns LC or MS conditions Other consumables, where allowed	• Sample preservation • QC requirements • Extraction procedure

- Follow specific information prescribed in the approved method
- Following any allowed modification, the laboratory must verify method performance by repeating IDC, verifying all QC in the method are met, and verifying method performance in a representative sample matrix
- Method modifications should be considered only to improve method performance, not simply shorten analysis time at the expense of performance
  - For example, chromatographic peaks should be reasonably resolved and symmetrical, while maintaining a minimum of 10 scans across the peak

PFAS Background Contamination

- Background contamination often observed at 0.1-0.5 ng/L without mitigation
- Potential sources include (though not limited to):
  - Instrumentation
  - Solvents/Reagents
  - Laboratory Materials
  - Air
- Reduce contamination by muffling or pre-cleaning all glassware and storing in resealable plastic bags
- Keep plasticware in resealable plastic bags
- Use a positive displacement pipettes with disposable tips
- Proper calibration (force through origin)
- Use delay columns (secondary columns to separate target analytes from interferences)

Analytical Method Development

- LC-MS/MS Direct Injection PFAS Method *(draft Method 534[#])*
- LC/MS/MS Direct Injection Ultra Short Chain PFAS Method
- LC/MS/MS Endothall and Glyphosate (*draft Method 561[#])*
- GC/MS urethane and methyl-2-pyrrolidone (*draft Method 558[#]*)
- EOF Total PFAS Drinking Water Method (ORD lead)

EPA is always looking for laboratories interested in participating in multi-lab validation studies

[#] *Though method numbers are assigned to these draft drinking water methods, they have not been published as method development is on-going.*

Drinking Water Method Approval

Expedited Method Approval Action – January 2024

- Ninety methods from 24th edition of *Standard Methods for the Examination of Water and Wastewater* (2023)
  - Methods were reviewed and compared to earlier versions of those methods that are currently approved in 40 CFR Part 141.
- ASTM D 3454-21 as updated version of the approved ASTM D 3454-97 for determination of radium-226 in water.
- Two Vendor Methods Evaluated Through the Drinking Water Chemistry ATP Program
  - Hach Method 10312 for determination of fluoride in finished water using planar cuvettes prefilled with colorimetric reagents.
  - Yokogawa Method 820 using 650-670 nm LED source for nephelometric determination of turbidity in finished water.

Drinking Water Method Approval

Drinking Water Method Update Rule (MUR)

- Expecting to release proposed DW MUR later this year
- Goals:
  1) Transfer methods approved under the Expedited Method Approval process from 40 CFR Part 141, Appendix A to Subpart C, to the respective regulatory method tables within the referenced regulation;
  2) Remove methods that are obsolete or do not meet the technological or quality standards of more recent compliance monitoring analytical methodology
  3) Clarify language and tables in 40 CFR Part 141 that are associated with drinking water analytical methodology or the analysis of drinking water contaminants and water quality parameters.

Unregulated Contaminant Monitoring Rule

- Objective is to collect nationally-representative occurrence data for unregulated contaminants that may warrant regulation under SDWA.
- https://www.epa.gov/dwucmr/learn-about-unregulated-contaminant-monitoring-rule

EPA's 5th Unregulated Contaminant Monitoring Rule (UCMR 5)

- Safe Drinking Water Act (SDWA) Section 1445(a)(2), as amended in 1996 and 2018, established requirements for the UCMR Program:
  - Issue a list of up to 30 priority unregulated contaminants in drinking water, once every 5 years
  - Require monitoring by all large PWSs (serving a population > 10,000) *and, subject to availability of appropriations and sufficient lab capacity, all PWSs serving 3,300 to 10,000*
  - Require monitoring for a nationally-representative sample of small PWSs serving ≤ 3,300
  - Make analytical results publicly available
  - EPA funds all shipping and analytical costs for small PWSs (serving <10K).

EPA's 5th Unregulated Contaminant Monitoring Rule (UCMR 5)

- EPA manages the program in partnership with States, Tribes, and Territories that volunteer to assist.
- Final Rule was published December 27, 2021.
- PWSs will collect samples 2023-2025.
- UCMR 5 addresses the following:
  - 29 PFAS (using EPA Methods 533 and 537.1)
    - 6 of the 29 were also part of UCMR 3
  - Lithium (using EPA Method 200.7, SM 3120 B, or ASTM D1976-20)

Public Access to UCMR 5 Results from Small and Large PWSs

- EPA publicly releases UCMR 5 results, a data summary report and updates an interactive Data Finder searchable database each calendar quarter.

- Provided results at a national level (e.g., the number of PWSs with results above the MRL and above health-based reference concentrations).

National occurrence data are publicly available at:
https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule

Questions?