EPA Method Development: Per- and Polyfluorinated Alkyl Substances

Christopher A. Impellitteri-EPA-Office of Research and Development
Schatzi Fitz-James-EPA-Office of Land and Emergency Management
Cynthia Caporale-EPA-Region 3

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Overview

- EPA method development
  - Safe Drinking Water Act (DW Methods)
  - Clean Water Act (CWA Methods)
  - Resource Conservation and Recovery Act (SW-846 Methods)

- Update on PFAS analytical method development and validation efforts

Safe Drinking Water Act-DW Methods

- Development/approval-through rule making (e.g. Unregulated Contaminant Monitoring Rule)
- Internal single-laboratory validation
- External multi-laboratory validation
  - Minimum 2 laboratories
- Draft method revisions
- Internal clearance process
- Internal and external peer-review
- Revision
- Office of Water Clearance
- Finalize and publish
- See https://www.epa.gov/dwanalyticalmethods

Clean Water Act Methods

- Development/approval through rule making
- Single lab validation with multiple water and wastewater (WW) matrices for relevant contaminants
  - Matrix types related to permit: WW effluent, biosolids, recreational water
- Multi-laboratory validation-usually 6 or more labs analyze multiple matrices
- EPA statistically derives detection limits and QC acceptance criteria from the multi-laboratory data

Clean Water Act Methods

- The Alternative Test Procedure (ATP) protocols contain a similar validation process. ATPs can only be used for analytes that are already regulated
  - See https://www.epa.gov/cwa-methods/alternate-test-procedures
- Once a method successfully undergoes multi-lab validation, it can only be approved through rulemaking
  - A rule is proposed with supporting documentation (e.g. the method, multi-lab study report, associated data packages)
  - Comments are received from the public
  - EPA responds to comments, which can result in minor revisions to the rule
  - Internal review of comment response and final rule (includes Office of Policy and Office of General Counsel)
  - Rule finalized (signed by the Administrator)
- See https://www.epa.gov/cwa-methods

SW-846 Methods

- Resource Conservation and Recovery Act-Method development and validation
  - https://www.epa.gov/hw-sw846/guidance-methods-development-and-methods-validation-resource-conservation-and-recovery-act
- 3 matrix types
- 7 replicates
- 2 spiking levels (in addition to background matrix)
  - Low (5X lower quantitation limit)
  - High (50X lower quantitation limit)
- GUIDANCE Methods, except for method defined parameters (MDPs) that are mandated by RCRA regulations (e.g. Toxicity Characteristic Leaching Procedure)
- No formal alternative test procedure protocols. More site-specific flexibility

Voluntary Consensus Standards

- Executive Office of the President-Office of Management and Budget (OMB)
  - Final Revision of OMB Circular A-119-Federal Participation in the Development and Use of Voluntary Consensus Standards and in Conformity Assessment Activities
  - Consistent with section 12(d) of P.L. 104-113, the "National Technology Transfer and Advancement Act of 1995"
- Directs agencies to use standards developed or adopted by voluntary consensus standards bodies rather than government-unique standards, except where inconsistent with applicable law or otherwise impractical

Voluntary Consensus Standards

- “Impractical” includes circumstances in which such use would fail to serve the agency's regulatory, procurement, or program needs; be infeasible; be inadequate, ineffectual, inefficient, or inconsistent with the agency mission or the goals of using voluntary consensus standards; be inconsistent with a provision of law; or impose more burdens, or be less useful, than the use of another standard

PFAS Method Development and Validation Update

- Drinking Water-Method 537
- Non-DW aqueous samples-SW-846 Draft Method 8327
  - Groundwater
  - Surface water
  - Wastewater effluent
- Non-DW aqueous and solids-SW-846 Draft Method 8328
  - Same aqueous matrices as 8327
  - Soils, sediments, biosolids
- ASTM D-7968

Drinking Water Method 537

- Six per- and polyfluorinated alkyl substances (PFAS) under the 3rd Unregulated Contaminants monitoring rule (UCMR3)
- Eight additional PFAS not listed on UCMR3
- Finished (treated) drinking water samples

Drinking Water Method 537

- Update: External lab validation for additional analytes by 537
  - Hexafluoropropylene oxide dimer acid (HFPO-DA, GenX chemical, CAS 13252-13-6)
  - 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS, CAS 756426-58-1)
  - 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS, CAS 763051-92-9)
  - 4,8-dioxa-3H-perfluorononanoic acid (ADONA, CAS 919005-14-4)
- Recruit external labs, ship samples, run multi-lab validation (complete)
- Draft method revision for peer review (end of October, 2018)
- Final published method as EPA Method 537.1 (November 2, 2018)

  Available at: *www.epa.gov/water-research/epa-drinking-water-research-methods*

Drinking Water New Method

- Solid phase extraction method targeting 25 PFAS compounds
  - Method targets “shorter chain” ($<C_{12}$) analytes that are compatible with weak anion exchange SPE to monitor additional PFAS, mostly outside the scope of 537.1
  - Method addresses select fluorotelomer sulfonates, perfluoroether compounds and PFBA
  - Office of Water targeting June 2019 for method completion

SW-846 Draft Method 8327

- Non-DW aqueous matrices (groundwater, surface water, wastewater effluent)
- Focuses on:
  - Simplicity
  - Robustness
  - Maximizing throughput for production lab use
  - Minimizing sample transfers, extractions, filter steps, chemical additions (e.g. pH adjustments)
- Find a balance among sensitivity, ease of implementation, and monitoring requirements

SW-846 Draft Method 8327

- 24 PFAS (including all target analytes in EPA Method 537)
  - Commercially available standards (“neat” and isotopically labeled)
- Direct injection based on EPA Region 5/Chicago Regional Laboratory Method
  - Similar to draft American Society for Testing and Materials (ASTM) Method D7979
  - Phase 1: 6 internal (EPA) lab validation
    - Completed December 2017
  - Phase 2: 10 external lab validation (ongoing)
    - Initial demonstration of capability complete
      - 7 labs “in”
      - 3 labs “out”
    - Shipped samples (60 unknowns: surface, ground, and waste waters) August 2018
    - January 2019 for draft method posted for public comment
- Target Quantitation Limits: 10 nanogram/L

SW-846 Draft Method 8328

- SW-846 Draft Method 8328
- More complex method relative to direct injection, however 8328 will
  - Likely be more robust for complex matrices (e.g. wastewater influents, biosolids)
    - Account for matrix effects (e.g. sorption) through isotopically marked standard recoveries
  - Afford options to meet DoD requirements
  - Allow users to perform a deeper dive based on screening (e.g. 8327) results

SW-846 Draft Method 8328

- SW-846 Draft Method 8328
- Same 24 PFAS analytes plus GenX chemical (HFPO-DA)
- Based on existing SOP that meets DoD Quality Systems Manual (QSM) 5.1 Table B-15 requirements
  - Many DoD requirements are optional for users that wish to use isotope dilution at non-DoD affiliated sites
- Surface, ground, and waste water plus solids (soils, sediments, biosolids)
- Target Quantitation Limits: 10 nanogram/L
- Build in flexibility
  - Columns
  - Elution schemes
- 2 lab internal validation started, 10 lab external validation study planned but…
  - Process is too slow. Exploring collaborative effort with DoD to jump start external laboratory validation. Target Spring 2019 for draft method.

ASTM D7968

- Soil extraction/direct injection
- 24 analytes
- Office of Land and Emergency Management collaboration with ASTM
  - External multi-laboratory validation

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For Further Research

- Total Organic Fluorine
- Total Oxidizable Precursors
- Non-targeted Analyses
- Tissues
- Air

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Questions? Comments?

- Contacts:
  - OLEM-Schatzi Fitz-James: fitzjames.schatzi@epa.gov
  - Region 3- Cynthia Caporale: caporale.Cynthia@epa.gov
  - ORD-Chris Impellitteri: Impellitteri.Christopher@epa.gov
  - Communications-Michelle Latham: latham.michelle@epa.gov