



Office of Research and Development

Massachusetts Department
of Environmental
Protection April 16, 2019
Lawrence, MA

SAFE AND SUSTAINABLE WATER RESOURCES RESEARCH PROGRAM

A graphic of a blue water splash with droplets, positioned horizontally across the middle of the slide.

EPA Method Development Update: Per- and Polyfluoroalkyl Substances (PFAS)

Ron Herrmann, Marc Mills, and Christopher A. Impellitteri
EPA/ORD



Disclaimer

The information in the EPA presentation has been reviewed and approved for public dissemination in accordance with U.S.

Environmental Protection Agency (EPA) policy. The views expressed in this presentation are those of the author(s) and do not necessarily represent the views or policies of the Agency.

Any mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.



Overview

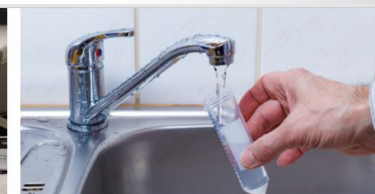
Drinking Water Revision 1 (537.1)

Drinking Water Draft Method 533

SW-846 8328

ASTM D7968

**Emerging techniques to determine
“Total” PFAS**





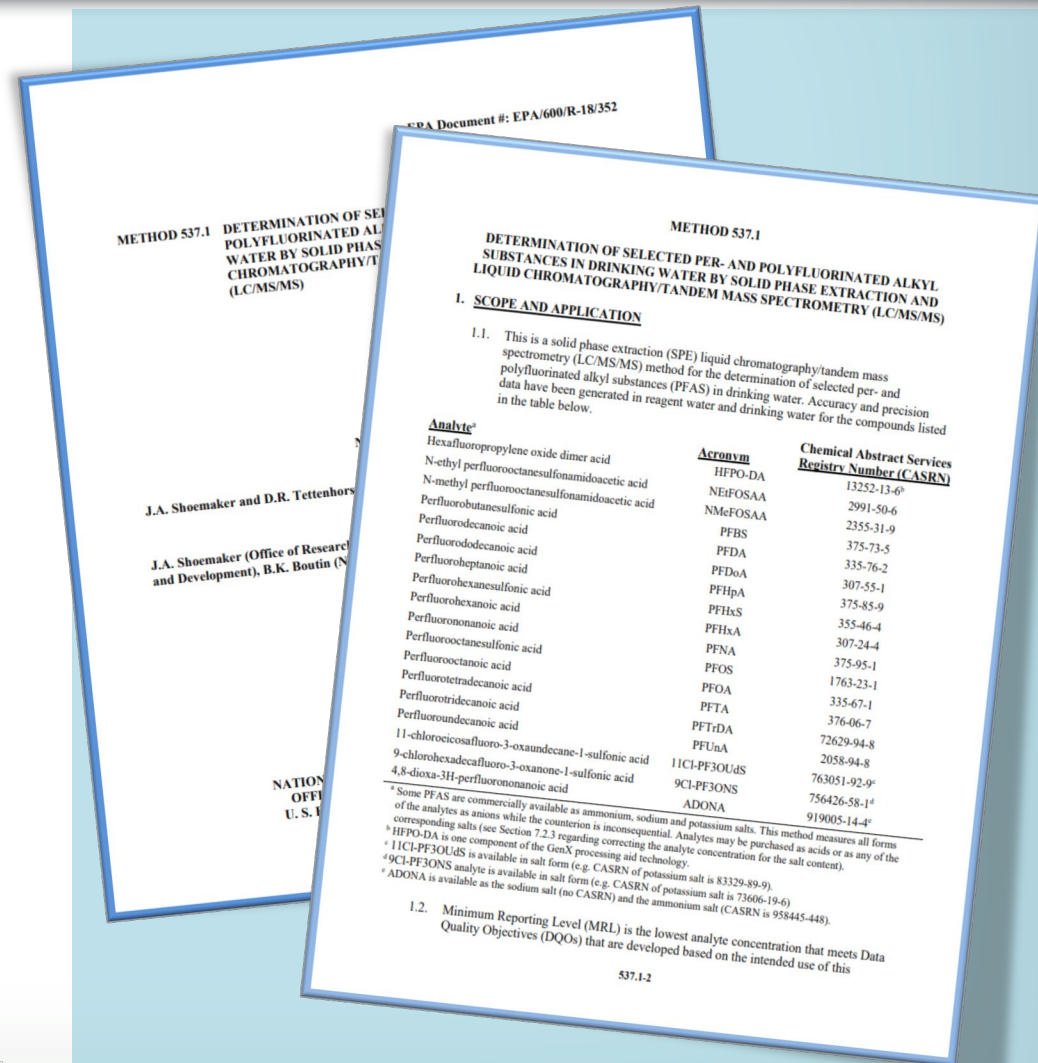
Drinking Water Method 537: Revision I

- **Update: External lab validation for additional analytes by 537**

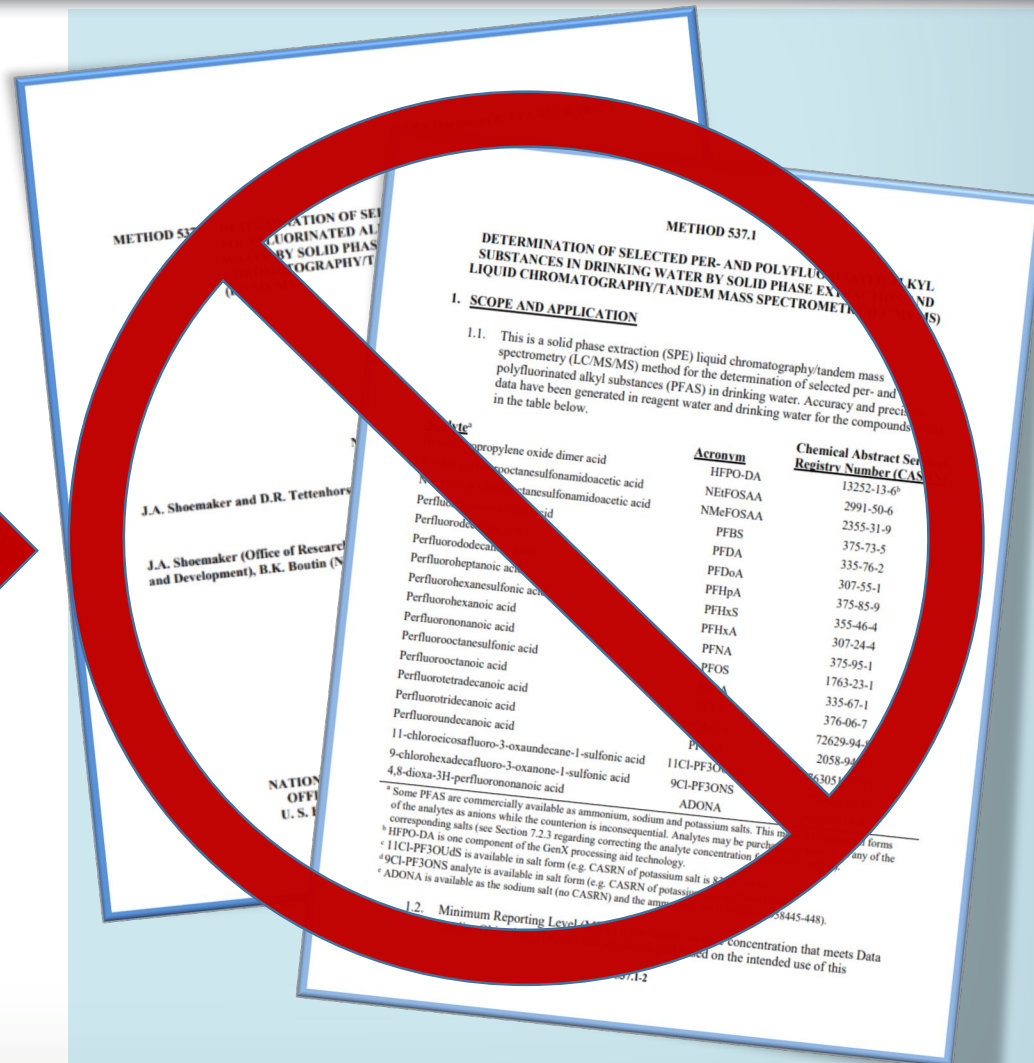
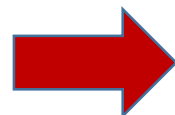
- Perfluoro-2-propoxypropanoic acid (GenX chemical HFPO-DA, CAS 13252-13-6)
- Potassium 9-chlorohexadecafluoro-3-oxanone-1-sulfonate (9Cl-PF3ONS, CAS 73606-19-6)
- Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS, CAS 83329-89-9)
- Sodium dodecafluoro-3H-4,8-dioxanone (ADONA, CAS 958445-44-8)

- **Incorporated clarifications issued in EPA Technical Advisory** epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf

- **Final published method (November, 2018)** epa.gov/water-research/epa-drinking-water-research-methods



- **Method 537 often modified by analytical laboratories for use on non-drinking water samples.**
- **If modifications are made that are not explicitly listed in 537 or 537 Revision 1, the method is not considered 537 by EPA.**
- **The most common modification is inclusion of isotope dilution.**





New Drinking Water Method 533: Under Development

Solid phase extraction/internal standard method targeting PFAS <C12

- **Method 537 generally performs poorly for C4 compounds (e.g. PFBA, PFBS).**
- **Method contains options for using isotope dilution or external standard calibration (or, possibly, two separate methods will be posted).**
- **EPA Office of Water targeting June 2019 for draft method for public comment.**





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8327—Direct Injection*

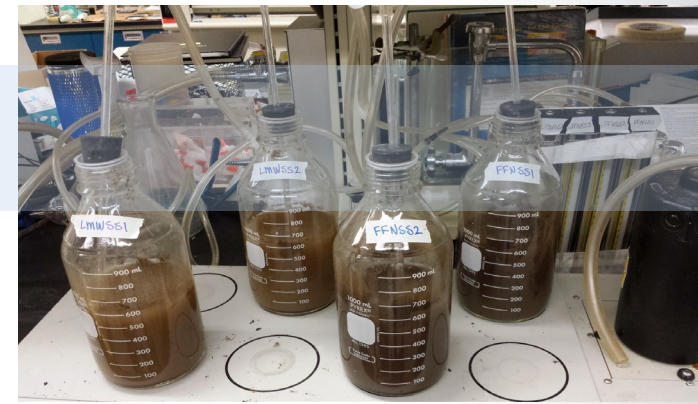
Non-drinking water aqueous matrices:

- Groundwater
- Surface water
- Wastewater

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.





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8327—Direct Injection*

24 PFAS (including all target analytes in EPA Method 537)

- Commercially available standards (“neat” and isotopically labeled)

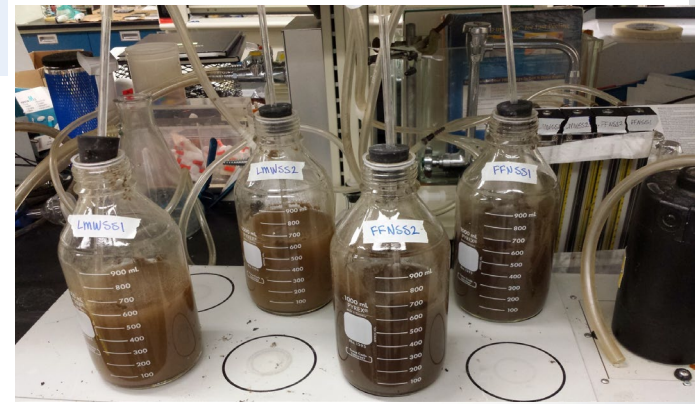
Direct injection based on EPA Region 5/Chicago Lab Method

- Similar to draft American Society for Testing and Materials (ASTM) Method D7979
- Multi-laboratory validation study completed in 2018
- Currently reviewing full data packages and conducting statistical analysis
- Currently Revising final draft

Post draft at the end of April 2019

(Depending on Office of Management and Budget review requirements)

Target Quantitation Limits: 10 nanogram/L





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8328—Isotope Dilution*

More complex method relative to direct injection, however 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; and
- allow users to perform a deeper dive based on screening (e.g. 8327) results.

Same 24 PFAS analytes plus GenX chemical (HFPO-DA)

Non-drinking water sources

- Surface water
- Groundwater
- Wastewater
- Solids (soils, sediments, biosolids)





Non-Drinking Water Sample Methods: *SW-846 Draft Method 8328—Isotope Dilution*

Based on existing SOP that meets DoD Quality Systems Manual 5.1 Table B-15 requirements

- Many DoD requirements are optional for users that wish to use isotope dilution at non-DoD affiliated sites.

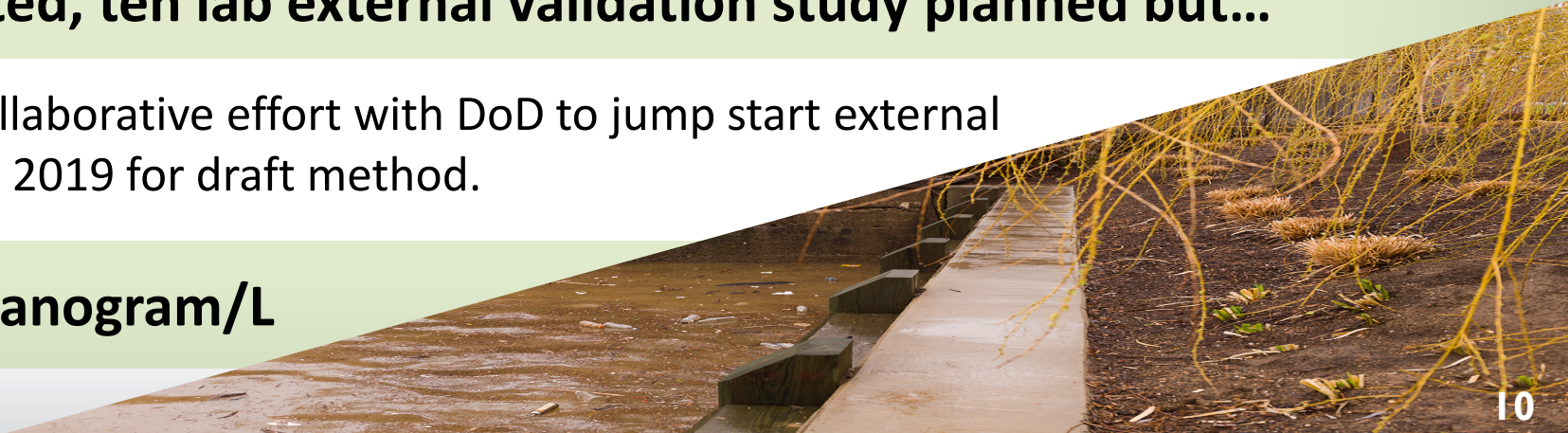
Build in flexibility

- Columns
- Elution schemes

Two lab internal validation started, ten lab external validation study planned but...

- Process is too slow. Exploring collaborative effort with DoD to jump start external laboratory validation. Target Fall 2019 for draft method.

Target Quantitation Limits: 10 nanogram/L



- Environmental solids: soil, sediment, sludge, etc.
- Solvent extraction, analysis by LC/MS/MS
- 30 target analytes
- 9 surrogate standards (isotopic-labeled target analytes): Used to monitor analytical method, not used to “correct” data
- Quantitation with 2 SRMs and ion ratios



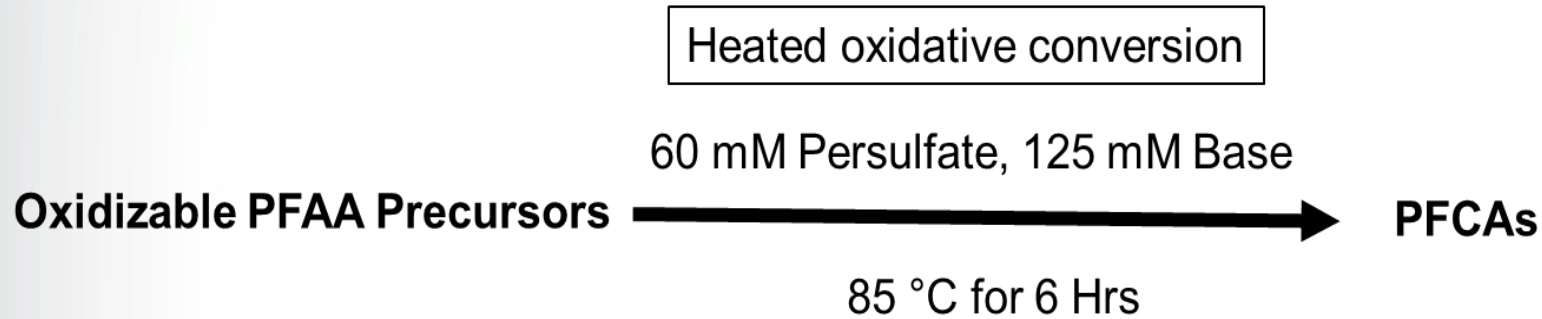


Emerging Techniques for “Total” PFAS

- **Total oxidizable Precursor Assay (TOP Assay)**
- **Total Organofluorine analysis using combustion ion chromatography (TOF)**
- **Non-targeted analysis**



Total Oxidizable Precursor Assay (TOP Assay)



$$\text{Total Oxidizable Precursors} = \text{PFCAs}_{\text{after oxidation}} - \text{PFCAs}_{\text{before oxidation}}$$

- Applicable for both aqueous and solid matrices
- Conservative estimate of the total concentration of PFAA precursors

- Does not identify individual precursor compounds
- More expensive technique - Sample needs to be analyzed 2 times for PFAAs – before and after oxidation
- Available in commercial labs and under evaluation at EPA, however, no standard methods currently exist.



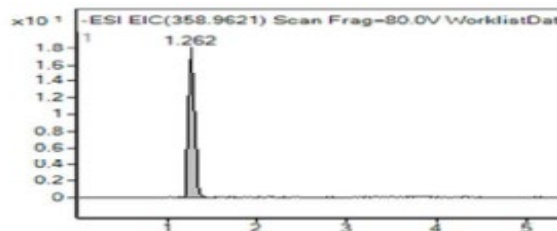
Total Organofluorine Analysis using Combustion Ion Chromatography (TOF)



- No specialized or costly instrumentation required
- Applied for aqueous matrices and blood samples
- Removing the background inorganic F^- from the sample is important to make sure that the reported F^- is organic
- Can be developed on a wide commercial scale

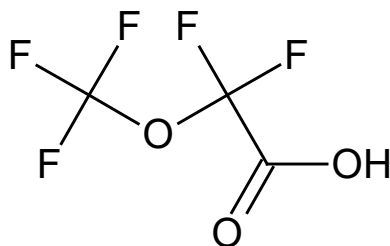
Explore Unknown compounds using High resolution mass spectrometry. Identify a peak in a chromatogram and to ultimately predict the identity of this unknown

↓ Mass spectrometer assigns a high resolution mass for peaks observed in the chromatogram



↓ Software calculates the exact number and type of atoms needed to achieve the measured mass.

↓ Fragmentation experiments allow determination of most likely structure:



Molecular Formula: C₃HF₅O₃
Monoisotopic Mass: 179.984585 Da
[M-H]⁻: 178.977308 Da

↓ Using mass, formula, and structure, identity can be assigned by searching against databases of known compounds

↓ Compare peak to commercial to confirm identification if possible



Contacts for Questions or Comments

- Ron Herrmann, ORD: Herrmann.Ronald@epa.gov
- Marc Mills, ORD: mills.marc@epa.gov
- Chris Impellitteri, ORD: Impellitteri.Christopher@epa.gov
- Schatzi Fitz-James, OLEM: fitzjames.schatzi@epa.gov
- Cynthia Caporale, Region 3: caporale.Cynthia@epa.gov
- Michelle Latham, Communications: latham.michelle@epa.gov