



Validated Analytical Methods for PFAS Measurement in Environmental Samples (Aqueous)

Jim Voit

Center for Environmental Solutions and Emergency Response Office of
Research and Development

Executive Meeting | Board of Scientific Counselors
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The views expressed in this presentation are those of the author(s) and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

- Validated analytical methods provide the means to collect data for research and regulatory applications
- Demonstrated and validated method performance in specific sample matrix types to collect data of known quality that is reproducible and defensible
- EPA standard methods are recognized nationally and internationally as the “gold standard” for analytical methodology by industrial, academic and other governmental agencies

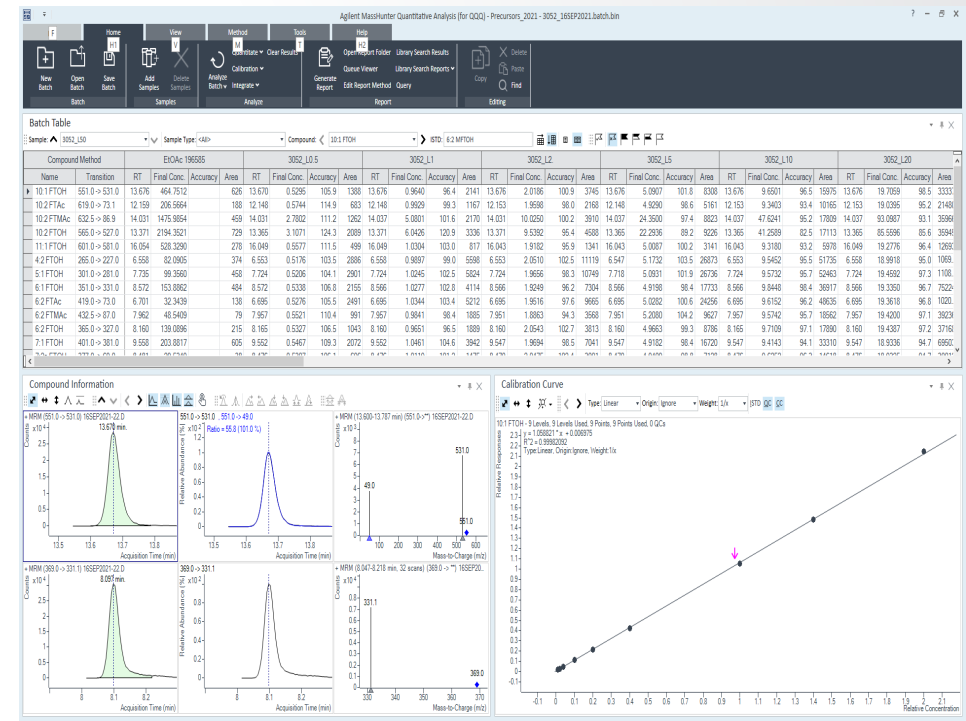
- Safe Drinking Water Act (SDWA) method developed by ORD for finished drinking water
- Revision 2 published March 2020
- 18 PFAS, including perfluorocarboxylic and sulfonic acids (chain length $\leq C14$), perfluoroethers (HFPO-DA), and sulfonamides
- Solid Phase Extraction, LC/MS/MS data acquisition, quantification by internal standard calibration technique
- Limit of Detection (LOD) capable of regulatory application to PFOA/PFOS advisory level





EPA 533

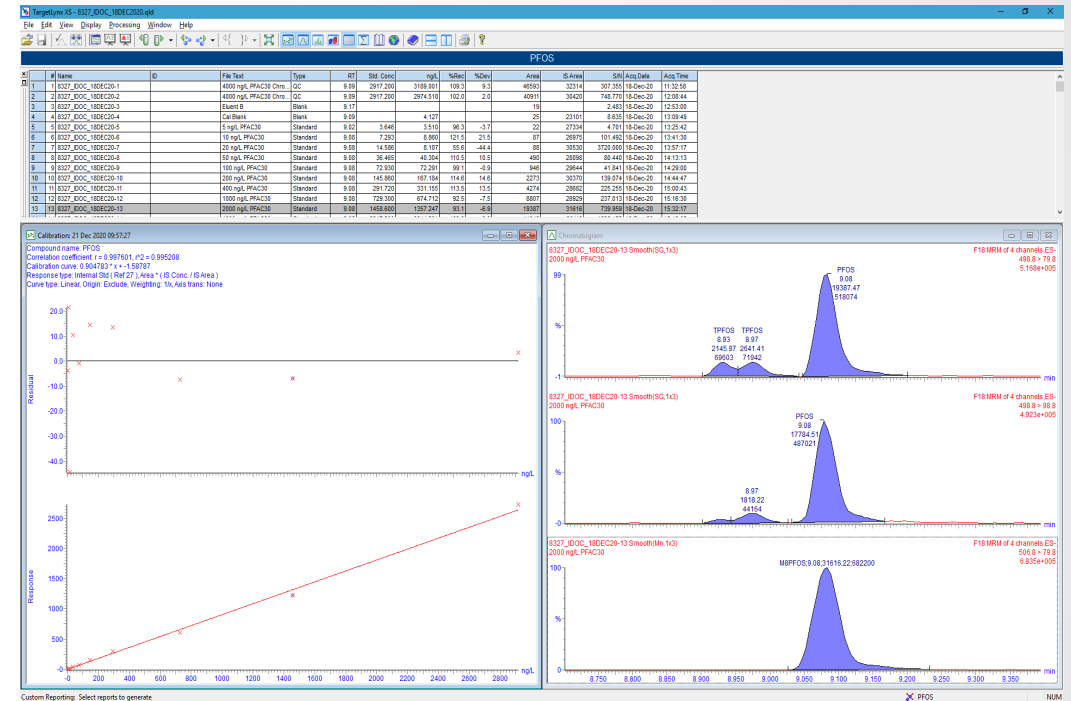
- Safe Drinking Water Act (SDWA) method developed by OW for drinking water, published November 2019
- 25 PFAS
 - C4 to C12 acids, perfluoroethers
 - Complements 537.1 to provide analytical capability for 29 PFAS in drinking waters
- Solid Phase Extraction, LC/MS/MS data acquisition, quantification by internal standard calibration technique (isotope dilution option)
- Limit of Detection (LOD) capable of regulatory application to PFOA/PFOS advisory level





SW846 Method 8327

- Methods 3512 (extraction) and 8327 (Analysis) published July 2021
- Method developed by R5/OLEM for 24 PFAS in non-potable water
- Direct Injection, LC/MS/MS data acquisition, quantification by external standard calibration technique
- A simple and robust high throughput analytical method for screening level characterization of surface water, groundwater, wastewater
- Limit of Detection (LOD) higher than the SDWA methods





Contributors

EPA 537.1: Office of Research and Development (ORD)

EPA 533: Office of Water lead, ORD contributor

SW846 Method 8327: Office of Land and Emergency Management, EPA Region 5, ORD contributor

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Analytical Method for PFAS in Environmental Media: CWA-1633

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PFAS Analytical Methods

- Drinking Water Methods
 - EPA 537.1
 - EPA 533
- Non-Drinking Water Methods
 - SW-846 Method 8327 – Direct Injection
 - Draft CWA-1633—Isotope Dilution
- PFAS Analysis in Marine Waters
- PFAS Analysis in Fish Tissue
- Total Organofluorine Analysis using Combustion Ion Chromatography (TOF)
- Total Oxidizable Precursors (TOP)
- Summary of EPA PFAS Methods as of April 2021



Types of Standard Methods

Three broad categories of EPA Standard Methods:

- [Safe Drinking Water Act Methods](#)
- [Clean Water Act Methods](#)
- [SW846 Methods](#)

These are generally targeted methods for solids and water.



Non-Drinking Water Sample Methods: CWA-1633/SW-846 Method—*Isotope Dilution*

Build in flexibility

- Columns
- Elution schemes

Single laboratory validated and released as draft CW-1633 in Sept 2021

- Collaborative effort among DoD, EPA Office of Water, EPA Office of Land and Emergency Management, and EPA ORD
- Multi-laboratory validation will start in 2021
- Method being developed in accordance SW-846 protocols for method development

Target Quantitation Limits: 1-10 nanogram/L

Matrices include:

- Wastewater (influent and effluent)
- Groundwater
- Surface water
- Landfill leachate
- Soil
- Sediment
- Biosolids
- Fish tissue





Non-Drinking Water Sample Methods: CWA-1633/SW-846 Method—*Isotope Dilution*

More complex method relative to direct injection; however, will:

- be more robust for complex matrices (e.g., wastewater influents, biosolids). Account for matrix effects (e.g., sorption) through isotopically-labelled standard recoveries;
- afford options to meet DoD requirements; and
- allow users to perform lower-level analyses based on screening results (e.g., 8327, TOF).

40 PFAS analytes - includes all analytes listed in 537.1, 533, and SW-846 8327

Non-drinking water samples

- Surface water, groundwater, wastewater
- Landfill leachates
- Solids (soils, sediments, biosolids, tissues)





Summary: EPA PFAS Methods, April 2021

EPA has validated Standard Methods complete or in development for PFAS in water

- Final SDWA Methods 533 and 537.1 for available for drinking water (29 PFAS)
- SW-846 Method 8327 validated for non-potable water (24 PFAS)
- Method in CWA-1633 completed single lab and undergoing multi lab validation for non-potable water/solids (40 PFAS). SW-846 determination to follow.

EPA has or is developing additional methods for partner use

- **Fish Tissue** – Isotope dilution method for 13 PFAS has been used in national surveys
- **Serum** – Isotope dilution method (targeted and non-targeted) used in biomonitoring
- **Ambient air and emissions** – Sampling and analysis methods undergoing development and testing
- **Total Organic Precursors (TOP)** – Identify total PFAS load which may degrade to most persistent PFAS
- **Total Organic Fluorine (TOF)** – Potential rapid screening tool to identify total PFAS presence/absence
- **Nontargeted analysis** – Continued development and application of HRMS methods for discovery of novel PFAS, suspect screening analysis, and identification of transformation and end products.



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Christopher Impellitteri, Andy Gillespie, and Susan Burden

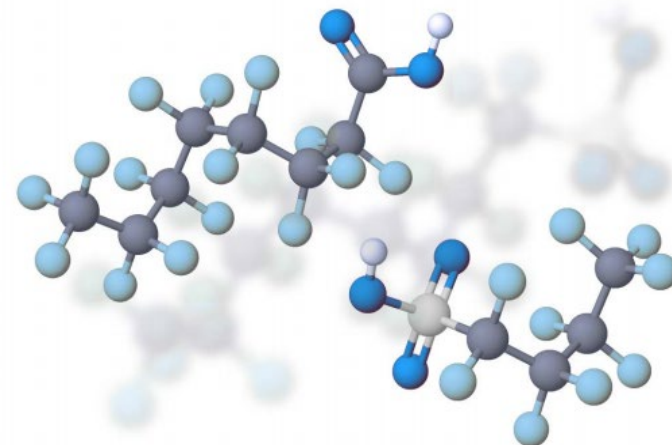
US EPA ORD

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EPA 823R18004 | February 2019 | www.epa.gov/pfas

EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan



U.S. Environmental Protection Agency



Development of Adsorbable Organic Fluorine (AOF) Screening Method with Detection by Combustion Ion Chromatography (CIC)

Jody A. Shoemaker and Jenifer L. Jones

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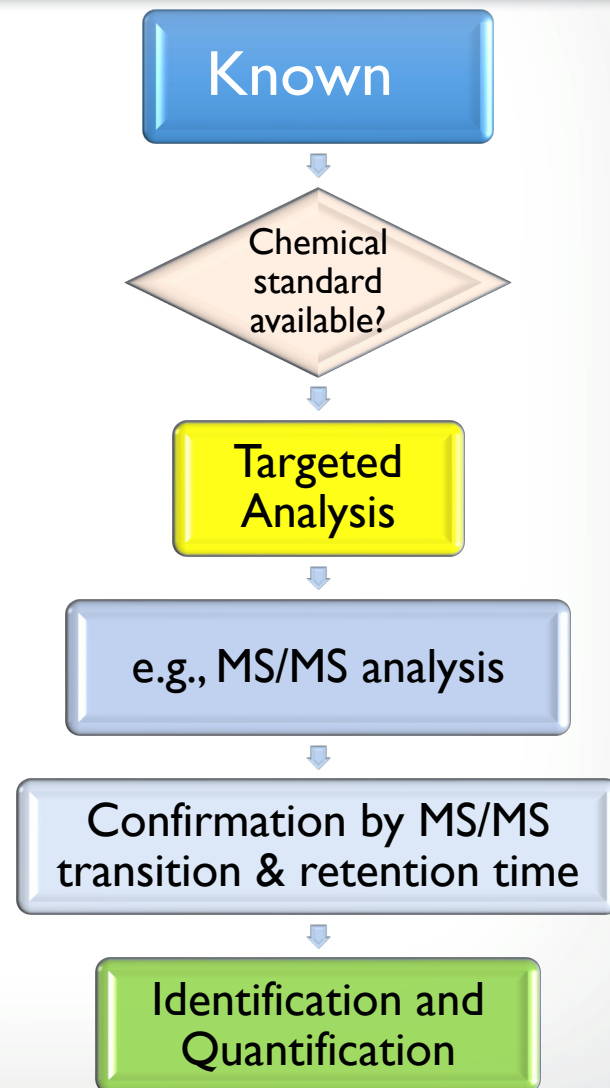


Why “Total PFAS” Methods?

Currently, most common PFAS detection technique is mass spectrometry (MS) using targeted analysis

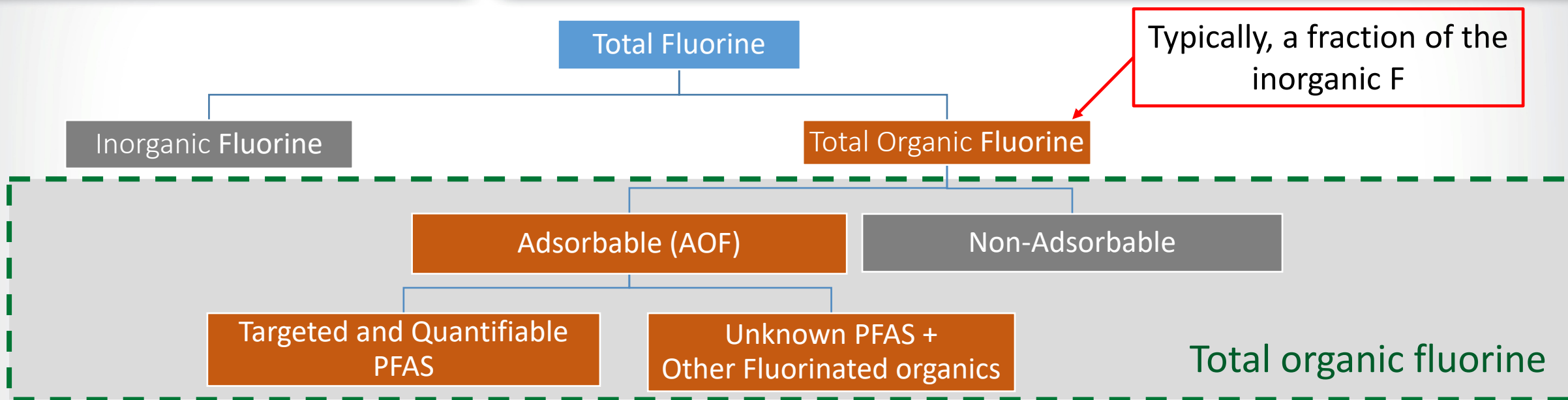
❖ Targeted Analysis:

- methods applicable to a specific defined set of known analytes
- analytical standards exist for quantitation
- methods only measure for analytes on the targeted list; once the analysis is complete, you can't look for other analytes.
- >4000 PFAS in existence





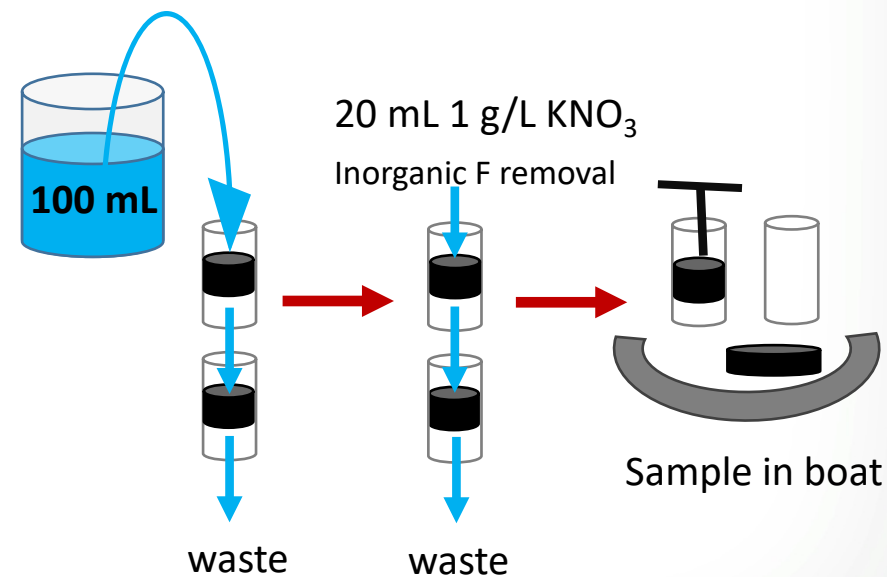
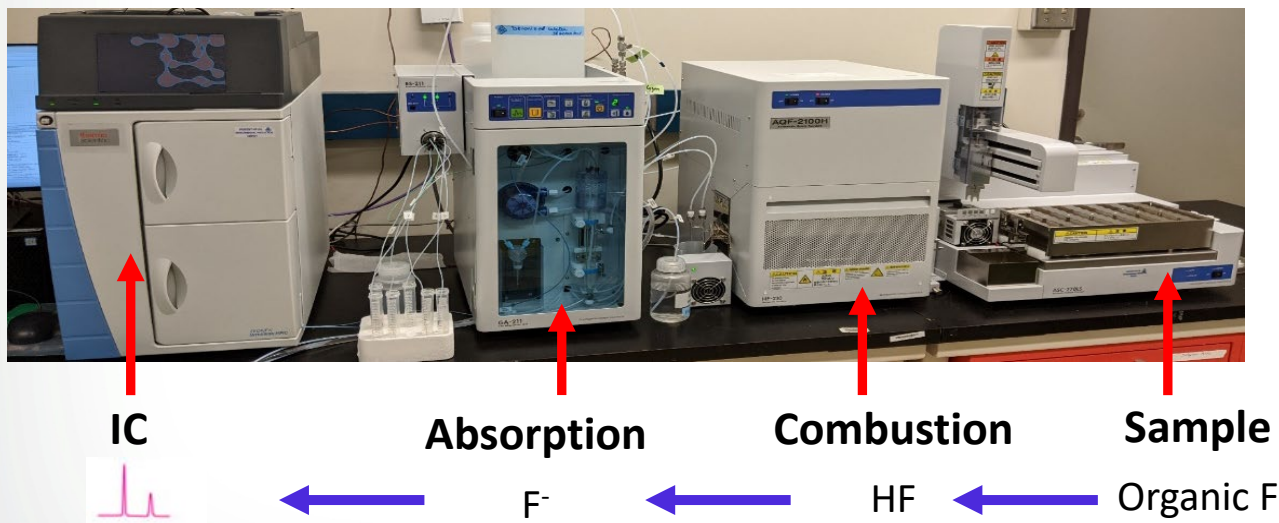
Goals



- Develop a screening method for wastewaters that measures adsorbable organic fluorine (AOF)
- Aid in screening for PFAS contamination or assessing removal of organofluorine contaminants in treatment streams
- AOF measurements must address removal of inorganic fluorine
- AOF measurements will include all adsorbable organic fluorine, e.g., fluorinated pharmaceuticals, agrochemicals

How:

- Screening method adsorbs contaminants onto granular activated carbon, removal of inorganic fluoride with nitrate solution, followed by combustion of the carbon
- Organofluorine compounds are converted to fluoride in the combustion process and measured by ion chromatography



Method Detection Limit: 1.4 - 2.2 µg/L



Current Status – AOF/CIC

Status:

- Recovery data for 35 PFAS, 2 PFAS mixtures, 4 fluorinated pesticides and pharmaceuticals
- Spiked recovery data in 14 wastewaters and 2 surface waters
- Delivery of draft wastewater screening method to OW by October 2021
- Multi-lab validation to be conducted by OW
- Submit manuscript for publication of AOF/CIC research by December 2021



Total Organic Fluoride for PFAS

Potential Future Work:

- To evaluate options that would lead to lower detection levels for the AOF/CIC method
- To keep an eye on other approaches that may come closer to capturing all PFAS within the method while not capturing inorganic fluoride or fluoride associated with other organic molecules (e.g., pesticides)
- Evaluate AOF/CIC technique for other matrices



Contributors

- Office of Research and Development

Jody Shoemaker, Jenifer Jones, Marc Mills, Tom Speth and Chris Impellitteri

- Office of Water

- Sarah Burket and Adrian Hanley

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