



Designation: E3302 – 23

Standard Guide for PFAS Analytical Methods Selection¹

This standard is issued under the fixed designation E3302; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide discusses the selection and application of analytical methods and techniques used to identify and quantify per- and polyfluoroalkyl substances (PFAS) in environmental media. This guide provides a flexible, defensible framework applicable to a wide range of environmental programs. It is structured to support a tiered approach with analytical methods, procedures, and techniques of increasing complexity as the user proceeds through the evaluation process. This guide addresses key decision criteria and best practices to aid users in achieving project objectives. There are numerous technical decisions that must be made in the selection and application of analytical methods and techniques used during environmental data acquisition programs. It is not the intent of this guide to define appropriate technical decisions, but rather to provide technical support within existing decision frameworks.

1.2 This guide informs practitioners on the considerations relevant to the selection and application of analytical methods and techniques for the quantitative and qualitative determination of PFAS in a variety of environmental sample media. This guide encourages user-led collaboration with stakeholders, including analytical laboratories, data evaluation practitioners, and regulators, in the selection and application of analytical methods and techniques used to support project-specific decision criteria and objectives as applied within a particular environmental regulatory program. This guide recognizes the complexity and diversity of environmental programs and project objectives and provides technical guidance for a range of project applications.

1.3 This guide is intended to complement, not replace, existing regulatory requirements or guidance. ASTM International (ASTM) guides are not regulations; they are consensus-based standards that may be followed as needed.

1.4 This guide recognizes that PFAS can be categorized as polymeric or nonpolymeric, collectively amounting to more

than 4 700 Chemical Abstracts Service (CAS)-registered substances. Environmental concerns pertaining to PFAS are centered primarily on the perfluoroalkyl acids (PFAA), a subclass of PFAS, which display extreme persistence in the environment and chain-length-dependent bioaccumulation and adverse effects in biota.

1.5 This guide recognizes that published analytical methods performed by commercial laboratories are limited to determination of a small subset of the more than 4 700 CAS-registered PFAS.

1.6 The goal of this guide is to provide a technical framework for informed selection and application of analytical methods and techniques for the determination of target and non-target PFAS in environmental sample media.

1.7 This guide aids users in selecting PFAS analytical methods for various environmental applications.

1.8 This guide discusses existing published analytical methods for quantitative determination of method-specific lists of target analytes, as well as non-standard analytical approaches developed to qualitatively determine a broader range of PFAS, for a variety of environmental applications. This guide also provides an overview of research trends in this rapidly developing field.

1.9 This guide discusses the challenges and limitations of analytical methods and techniques in the detection and quantitation of the large, complex set of PFAS.

1.10 This guide describes widely accepted considerations and best practices used in the selection and application of analytical procedures used during PFAS environmental programs. This guide complements but does not replace existing technical guidance and regulatory requirements.

1.11 *Units*—The values stated in SI units are to be regarded as the standard.

1.11.1 Other units, such as fractional units of parts per billion and parts per trillion, are also included in this guide.

1.12 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

¹ This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment, Risk Management and Corrective Action and is the direct responsibility of Subcommittee E50.04 on Corrective Action.

Current edition approved Dec. 15, 2023. Published January 2024. Originally published in 2021. Last previous edition approved in 2021 as E3302–21. DOI: 10.1520/E3302–23

1.13 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D7968 Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

D7979 Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

D8421 Test Method for Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Matrices by Cosolvation followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

2.2 USEPA Documents:³

EPA QA/G-4 Guidance on Systematic Planning Using the Data Quality Objectives Process, February 2006

EPA/600/F-17/022e PFAS Methods and Guidance for Sampling and Analyzing Water and Other Environmental Media – Technical Brief, February 2019, EPA/600/F-17/022h, updated January 2020

USEPA 815-B-16-021 Technical Advisory – Laboratory Analysis of Drinking Water Samples for Perfluorooctanoate (PFOA) Using EPA 537 Rev. 1.1, September 2016

USEPA Method 537 Version 1.1 Determination of Selected Perfluorinated Alkyl Acids (PFAAs) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) EPA/600/R-08/092, 2008, revised 2009.

USEPA Method 537.1 Version 2.0 Determination of Selected Per- and Polyfluorinated Alkyl Substances (PFAS) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) EPA/600/R-20/006, March 2020.

USEPA Method 533 Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), 815-B19-020, December 2019.

USEPA Test Method 8327 Per- and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Revision 0, July 2021

USEPA Draft Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, First Draft, EPA 821-D-21-001, August 2021; Second Draft, EPA 821-D-22-001, June 2022; Third Draft, EPA 821-D-22-003, December 2022; Fourth Draft, EPA 821-D-23-001, July 2023.

USEPA Draft Method 1621, Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC), EPA 821-D-22-002, April 2022.

U.S. Environmental Protection Agency PFAS Master List of PFAS Substances. CompTox Chemistry Dashboard, Version 2.2.1, May 2023, Available Online at: <https://comptox.epa.gov/dashboard/>

U.S. Environmental Protection Agency Drinking Water Health Advisories for Perfluorooctanoate (PFOA) and Perfluorooctane Sulfonate (PFOS), 822-R-16-004, 2016

U.S. Environmental Protection Agency Lifetime Health Advisories and Health Effects Support Documents for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS), Federal Register, Vol 81, No. 101, May 25, 2016

U.S. Environmental Protection Agency, Lifetime Drinking Water Health Advisories for Four Perfluoroalkyl Substances (PFOA, PFOS, GenX, and PFBS), Federal Register Vol. 87, No. 118, June 21, 2022.

U.S. Environmental Protection Agency, PFAS National Primary Drinking Water Regulation Rule Proposal (for PFOA, PFOS, PFNA, HFPO-DA or GenX Chemicals, PFHxS, and PFBS), Federal Register Vol. 88, No. 60, March 29, 2023.

U.S. Environmental Protection Agency, PFAS National Primary Drinking Water Regulation Rule Proposal (for PFOA, PFOS, PFNA, HFPO-DA or GenX Chemicals, PFHxS, and PFBS), Federal Register Vol. 88, No. 60, March 29, 2023.

2.3 ISO Documents:⁴

ISO 25101 Determination of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Water – Method for Unfiltered Samples Using Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC-MS/MS), 2009.

ISO 21675 Determination of Polyfluorinated Alkyl Substances (PFAS) in Water – Method Using Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC-MS/MS), 2019.

3. Terminology

3.1 Definitions:

3.1.1 *adsorbable organofluorine (AOF)*, *n*—a fraction of organofluorine that will sorb to a particular media, for example carbon, and that remains sorbed to the media after removal (washing) of the inorganic fluoride.

3.1.2 *combustion ion chromatography (CIC)*, *n*—a technique that combines pyrolysis of a sample and analysis of the combustion products using ion chromatography.

3.1.3 *extractable organofluorine (EOF)*, *n*—the fraction of organic fluorine that is first extracted and then analyzed.

3.1.4 *fluoride ion*, *n*—the inorganic anion of fluorine (F⁻); that is, fluoride.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

⁴ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.