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Standard Guide for PFAS Analytical Methods Selection[1]

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1. Scope

1.1 This guide discusses the selection and application of analytical methods and techniques used to identify and quantitate 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.

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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 Co-solvation 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 20211;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.

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.

3.1.5 *fluorides, n*—any compound containing fluorine are categorically deemed fluorides.

3.1.6 *fluorine (F), n*—a chemical element, diatomic form (F2); it is a highly toxic gas, reactive, and yellow-green in color.

3.1.7 *liquid chromatography mass spectrometry / mass spectrometry (LC/MS/MS; also known as triple quadrupole or triple quad LC/MS), n*—an analytical instrument that laboratory methods use to separate, identify, and quantitate specific targeted organic compounds.

3.1.8 *per- and polyfluoroalkyl substances (PFAS), n*—a group of manufactured chemicals consisting of polymeric chains of carbon bonded to fluorine atoms, usually with a polar functional group at the head.

3.1.8.1 *Discussion*—PFAS are fluorinated substances with a carbon chain structure. In perfluoroalkyl acids (PFAAs), each carbon atom in the chain is fully saturated with fluorine (carbon-fluorine bonds only), whereas the carbon chain in polyfluoroalkyl substances is mostly saturated with fluorine (carbon-fluorine bonds), but also contains carbon-hydrogen bonds.

3.1.9 *perfluoroalkyl acids (PFAA), n*—a subclass of PFAS including sulfonic and carboxylic acids that display extreme persistence and chain-length-dependent bioaccumulation and adverse effects in biota.

3.1.10 *precursor, n*—a category of PFAS that includes all polyfluorinated alkyl substances and a subset of polymer PFAS known as side-chain fluorinated polymers, collectively known as "precursors" because of their ability to transform into terminal defluorinated alkyl substances.

3.1.11 *proton-induced gamma-ray emission (PIGE), n*—a rapid screening technique that provides a qualitative and quantitative measure of total fluorine.

3.1.12 *quadrupole time of flight (Q-TOF), n*—an accurate MS/MS instrument that replaces the final quadrupole with a time-of-flight (TOF) high-resolution mass spectrometer.

3.1.13 *solid phase extraction (SPE), n*—a type of sample preparation that extracts targeted analytes from an aqueous matrix onto a solid medium, allowing the analytes to be separated from the matrix and subsequently eluted and concentrated in an organic solvent.

3.1.14 *total fluorine (TF), n*—a measure that includes organic and inorganic fractions of fluorine.

3.1.15 *total organic fluorine, n*—a measure of the total organic fraction of fluorine in a sample.

3.1.15.1 *Discussion*— Total Organic Fluorine is the description of the category and measurement, but not all CIC-dependent approaches can report a result that truly represents total organic fluorine. The reason being when a sample is extracted, adsorbed, or otherwise manipulated prior to combustion, the percentage of the total that is amenable to the extraction, adsorption, or manipulation (and thus quantified) is directly dependent on the approach used. Each approach has documented limitations. See guide Section 8 for more information.

3.1.16 *total oxidizable precursor (TOP), n*—a measure of oxidizable precursors determined by method-defined assays. In this context, the precursors are limited to PFAA precursors. The analytical method that quantifies the precursors is widely known as TOP Assay.

3.1.17 *total PFAS, n*—a surrogate estimate based on various analytical techniques of the summation or total value of TOP assay or total organic fluorine.

4. Significance and Use

4.1 This guide provides an overview of analytical methods, techniques, and procedures that may be used in determination of PFAS in environmental media.

4.2 This guide provides considerations relevant to the selection and application of PFAS analytical methods, techniques, and procedures, including the limitations of published analytical methods and the potential benefits and challenges of non-standard analytical approaches.

4.3 This guide presents comparisons of published analytical methods and approaches, including tabular comparison of target analyte lists and method features, to aid users in the selection and application of analytical methods and techniques for project-specific applications.

4.4 This guide describes qualitative techniques available to determine total PFAS, including explanation of terms, discussion of preparation and analytical techniques and limitations, conceptual overview schematic, and summary comparison table.

4.5 This guide provides current information on research trends in PFAS determination techniques applied to environmental media.

4.6 This guide provides an integrated framework that results in efficient, cost-effective decision-making for timely, appropriate response actions for PFAS-impacted environmental media.

4.7 This guide is not intended to replace or supersede federal, state, local, or international regulatory requirements. Instead, this guide may be used to complement and support such requirements.

4.8 This guide may be used by various parties involved in response actions for PFAS-impacted environmental media, including regulatory agencies, project sponsors, environmental consultants and contractors, site remediation professionals, analytical testing laboratories, data reviewers, data users, academic institutions, research institutes, and other stakeholders.

4.9 The users of this guide should consider assembling a team of experienced professionals with appropriate expertise to scope, plan, and execute PFAS environmental data acquisition activities.

4.10 The users of this guide should review the overall structure and components of this guide before proceeding with use, including the following sections:

4.10.1 Section 1: Scope

4.10.2 Section 2: Referenced Documents

4.10.3 Section 3: Terminology
4.10.4 Section 4: Significance and Use
4.10.5 Section 5: Project Planning Considerations
4.10.6 Section 6: Analytical Method Selection Considerations
4.10.7 Section 7: Analytical Methods Comparison
4.10.8 Section 8: Qualitative Techniques to Determine Total PFAS
4.10.9 Section 9: Research Trends
4.10.10 Section 10: Keywords
4.10.11 Appendix X1: PFAS Analytical Interferences – A Summary of Considerations

5. Project Planning Considerations

5.1 This guide complements applicable existing guidance used to develop a Quality Assurance Project Plan (QAPP) and to establish data quality objectives (DQOs) necessary to meet project goals and to evaluate data quality. This process encourages planners to identify and focus on the key issues and elements necessary for successful, cost-effective, and defensible project outcomes.

5.2 *Data Quality Objective Process:*

5.2.1 An important functional aspect of project planning is the DQO process. It is necessary to formalize these planning steps to ensure the type, quantity, and quality of PFAS data used in decision-making. Thoughtfully derived DQOs provide the qualitative and quantitative framework by which data collection activities are successful in terms of achieving project objectives. The qualitative aspect of DQOs seeks to encourage good planning for field investigations. The quantitative aspect of DQOs involves designing an efficient field investigation that reduces the possibility of incorrect decision-making.

5.2.2 The DQO process is defined in *Guidance on Systematic Planning Using the Data Quality Objectives Process* (USEPA 2006). The DQO process consists of seven steps as presented in 5.2.3 through 5.2.9, and each step is followed by specific examples (presented in *italics*). Included in the step descriptions are simplistic (not intended to be complete) example project circumstances involving the collection of PFAS groundwater data. Note that every project is different, and the DQO process should yield project-specific objectives.

5.2.3 **Step 1: State the Problem.** Define the problem that motivates the study; identify the planning team; and examine the budget and schedule.

5.2.3.1 *The state agency has required that the groundwater wells at our facility include a round of PFAS sampling and analysis.*

5.2.3.2 *Our environmental manager is working directly with our consultant and laboratory project managers.*

5.2.3.3 *Our consultant and laboratory have quoted $46,000, which includes final reporting to the state agency.*

5.2.3.4 *We are required to issue a final report before the end of this calendar year.*

5.2.4 **Step 2: Identify the Goal of the Study.** State how the PFAS data will be used to meet objectives and solve the problem, identify study questions, and define alternative outcomes.

5.2.4.1 *This study will determine whether our groundwater has PFAS. If PFAS target analytes are not detected above the state's new action limit, we have met our goal. If PFAS target analytes are detected above the state's new action limit, then additional sampling and source identification/control will likely occur.*

5.2.5 **Step 3: Identify Information Inputs.** Identify data and information needed to answer study questions.

5.2.5.1 *Groundwater levels and contour maps will be reviewed to select the proper number and locations of the wells to be sampled.*

5.2.5.2 *The special precautions associated with PFAS sampling, method requirements and associated sample volume requirements, the QC samples, and the specific list of PFAS target analytes the state is requiring need to be reviewed with the planning team.*

5.2.6 **Step 4: Define the Boundaries of the Study.** Specify the target population and characteristics of interest and define the scope and limitations of the study (that is, the study will not consider potential non-targeted analytes).

5.2.6.1 *The state's requirements are limited to the sampling and analysis of on-site monitoring wells.*

5.2.6.2 *We need to propose a reasonable number and locations of the wells to be sampled to the state. One or two upgradient wells will be considered.*

5.2.7 **Step 5: Develop the Analytic Approach.** Define the analytical parameters of interest; specify the type of inference and develop logic for drawing conclusions from the findings.

5.2.7.1 *The list of specific PFAS target analytes needs to be reviewed with the state agency and our contract laboratory. The method reference and any modifications need to be reviewed and approved. Reporting limits capable of ruling out the state's new action limits and the inclusion/omission of branched isomers need to be finalized with the contract laboratory.*

5.2.7.2 At this stage in the process, consider augmenting the study to include analysis of non-targeted PFAS (that is, "total" PFAS).

5.2.8 **Step 6: Specify Performance or Acceptance Criteria.** Develop performance criteria for new data being collected and acceptance criteria for data already collected.

5.2.8.1 *Through this sampling and analytical event, if PFAS target analytes are not detected above state action limits, then we will not have to include PFAS target analytes in future monitoring. If PFAS target analytes are detected above state action limits, then additional characterization, source identification/minimization and/or remediation could be future activities.*

5.2.9 **Step 7: Develop the Detailed Plan for Obtaining Data.** Select the most resource-effective work plan or Sampling and Analysis Plan (SAP) that satisfies the performance or acceptance criteria.

5.2.9.1 *After preliminary discussions with the state agency, we will meet with our consultant and contract laboratory, and our consultant will draft a SAP with input from the planning team members. The SAP will be reviewed and approved by the state before sampling activities proceed.*

5.3 *Project Data Quality Objectives:*

5.3.1 One of the decisions to be made when developing DQOs for a PFAS project is determining if the resulting analytical data need to meet performance or acceptance criteria. If PFAS data are to be used for screening-level analyses or pilot studies, for example, the level of data quality and the level of data evaluation conducted on the analytical data set may not need to be as rigorous as the PFAS data quality needed to meet legally enforceable standards and regulatory compliance applications.

5.4 *Regulatory Considerations:*

5.4.1 Regulatory stakeholders at the federal and state levels have used various mechanisms to establish PFAS limits for environmental media, from non-enforceable health advisory levels (HAL), guidance levels, and screening values to legally enforceable regulatory compliance criteria such as drinking water maximum contaminant levels (MCLs). Many regulatory agencies have developed PFAS regulatory limits for individual compounds, and some regulatory agencies have designed guidance and limits based on the summation of select PFAS.

5.4.2 Regulatory agencies implement accreditation and certification programs that govern laboratory sample processing and data reporting activities. Experienced laboratories have secured these accreditations and certifications using sophisticated sample extraction and analysis protocols to report specific PFAS target analytes in select sample media using both published analytical methods and laboratory proprietary analytical approaches. Project planners are encouraged to consider the regulatory accreditations and certifications available (by analyte, by method, and by sample matrix) and, when necessary, to engage the laboratory to consider analytical options where regulatory certification or accreditation may not be offered. Project planners and data users should confirm that laboratory accreditation or certification meets project objectives and regulatory requirements.

5.5 *Project Planning Considerations:*

5.5.1 The project QAPP is used to document decisions made in the consideration a range of elements considered in planning a PFAS data acquisition project. Elements typically considered during project planning include the following:

(1) Regulatory program requirements

(2) Regulatory criteria and project action limits (such as generic screening levels, site-specific criteria, and enforceable regulatory compliance standards)

(3) Laboratory certification and accreditation requirements

(4) Project DQOs

(5) Quality assurance (QA) and quality control (QC) requirements

(6) QAPP and SAP development and regulatory approval

(7) Data review, evaluation, validation, application, and uses

(8) Analytical chemistry approach (such as target analyte list, sample preparation protocols, analytical instrumentation, analytical method, data reporting, QC excursions, and data reporting format)

(9) Sample media (such as potable water, groundwater, surface water, effluent, soil, sediment, biological tissue, and environmental waste)

(10) Sample processing issues (such as concentrations of target and non-target analytes, sample matrix interference, sensitivity, levels of detection and quantitation, dilutions, re-runs, and QC excursions) (See Appendix X1).

(11) Turnaround time (for example, project schedule expectations, sample preservation and handling, sample hold times, analytical sequence, laboratory capacity, and sample re-runs)

(12) Data deliverable formats

5.5.2 This is not meant to be an exhaustive list, but a typical set of project planning considerations that inform decisions that enhance successful project outcomes.

5.6 *Data Acquisition Considerations:*

5.6.1 Communication within the project team, including the laboratory, is key to planning and executing a successful PFAS sampling event. Increased risk of cross-contamination requires PFAS-specific sampling procedures and a series of field QC samples. This is due to the persistence and surface-sorbing tendency of certain PFAS, as well as their ubiquitous presence in many products and materials.

5.6.2 The selection and handling of sampling equipment and materials (provided by the practitioner) and sample containers and blank water (provided by the laboratory) should be carefully considered during the planning and execution of PFAS field sampling programs. These items should not contain PFAS at concentrations that will interfere with the proposed analysis.

5.6.3 Field QC samples should be included in the design and execution of a PFAS sampling program. Field QC samples typically include equipment blanks (EB), field reagent blanks (FRB), field duplicates (FD), and project-specific matrix spike/matrix spike duplicate samples. Each of these field QC samples requires sufficient sample volume to fill a separate container, because these samples are individually processed and reported as part of the project data set.

5.6.4 Laboratory subsampling should not be performed because it may cause a low bias for large PFAS (>C10 perfluoroalkyl carboxylic acids, >C8 perfluoroalkyl sulfonic acids). These considerations should be documented in the project QAPP.

5.6.5 Application of PFAS analytical methods designed for a drinking water sample matrix to non-potable water samples should be discussed with the laboratory in advance of sample collection. Consideration should be given to the intended purpose of the preservative listed in method, which is to buffer chlorine added to treated finished drinking water supplies. The buffer is also essential to the SPE process by extraction of all samples at the same pH. When a drinking water method is applied to a non-drinking water sample matrix (such as groundwater or surface water), the decision regarding the sample preservative should be documented in the project QAPP and SAP.

5.6.6 The laboratory may experience QC non-conformances when processing untreated source water samples, which may contain elevated levels of suspended solids (turbidity), when applying an analytical method designed for treated finished drinking water. This may result sample reprocessing (that is, re-analysis of the sample extract or re-extraction of the original

sample) to confirm the initial result, which then results in extended turnaround time necessary to report final data.

5.7 *Performance Evaluation Samples—Single Blind and Double Blind:*

5.7.1 The use of performance evaluation (PE) samples is an important QC component that environmental practitioners should consider including in their environmental investigations. These known reference samples provide valuable information regarding the accuracy and comparability of laboratory data when one or more laboratories are being used. When possible, it is preferable to issue these samples double-blind to the project laboratories, meaning the receiving laboratories have no idea that they are analyzing a test sample. This can be accomplished by simply having an accredited PE sample vendor prepare the sample(s) in ordinary sample bottles, such as those prepared for investigatory sampling. The practitioner then labels (and separately documents) the sample with a fictious sample identification. It is critical when performing these double-blind studies that the accredited PE sample vendor certify the PFAS values in their whole-volume PE preparation.

5.7.2 When using a single-blind PE sample, the receiving laboratories know they are receiving test samples (either whole volume or ampulated), but they do not know the specific analytes and the true (vendor-certified) concentrations.

5.7.3 Essentially, the purpose of PE studies is to determine whether the laboratory can get the "right answer" on what appears to be a routine investigatory sample. When available, PFAS solid-matrix performance test (PT) samples, solid-matrix PFAS PE samples, and solid-matrix PFAS certified reference materials (CRM) will provide a means to evaluate the solid extraction and analytical procedures for PFAS. These standardized test materials could identify the ability of different laboratories to reproduce PFAS analytical results regardless of their "accreditation" status. This is currently an issue because laboratory PFAS procedures vary widely, and multi-laboratory-validated analytical methods for PFAS in non-drinking water sample matrices are limited.

5.8 *Calibration Standards—Primary Source and Secondary Source:*

5.8.1 For PFAS laboratory calibration and QC, the number of PFAS and the vendors who create these analytical standards and reference materials are limited. In 2020, there were two standard vendors who provide analytical reference material for analysis of PFAS in drinking water through USEPA Method 537.1 and Method 533, as well as for analysis of PFAS in non-drinking water and solids through other methods with extended PFAS target analyte lists. Due to the limited availability of standards, laboratories are not always able to use a true second-source standard to verify their calibration, which is why USEPA Method 533 does not currently require second-source verification of initial calibration curves. When analytical standards and reference materials are available, some laboratories may use a standard from a second vendor as a second-source verification. However, due to the limited availability of PFAS standards, many will use different lots or single-component standards from the same vendor to verify their initial calibration curves.

5.9 *Quantitation of Branched and Linear Isomers:*

5.9.1 Individual PFAS can exist as linear and branched isomers. Ideally, the concentration of a given PFAS would include the linear isomer, which is usually but not always the case, together with any associated branched isomers to provide a total concentration for that analyte. While the current practice is for laboratories to report a single total concentration, (if qualitative and/or quantitative standards exist for the branched isomer components.),there is growing interest in identifying and reporting the linear and branched isomers separately although there are a number of technical challenges with this reporting (such as the lack of chromatographic resolution criteria within the existing methods). However, at the time of this writing, limited suitable quantitative standards containing both linear and branched standards exist for only four common PFAS: perfluorooctane sulfonate (PFOS), perfluorohexane sulfonic acid (PFHxS), *N*-ethyl perfluorooctane sulfonamido acetic acid (NEtFOSAA), and *N*-methyl perfluorooctane sulfonamido acetic acid (NMeFOSAA). When USEPA Method 537 was promulgated in 2009, it specified that both linear and branched isomers be included in the calibration and quantification of these compounds. A technical grade standard for perfluorooctanoate (PFOA), which included branched isomers was available at the time leading to some laboratories including PFOA branched isomers while others did not. To clarify this requirement, USEPA issued a technical advisory (USEPA 2016, EPA 815-B-16-021) for USEPA Method 537 that specifically identifies PFOS, PFHxS, NEtFOSAA, and NMeFOSAA as containing branched isomers and requires that quantitative standards be used to correctly identify and quantitate all chromatographic peaks for these compounds (note that more recent data suggests that other PFAS may also include branched and linear isomers). The advisory further addressed PFOA, stating that the technical grade standard should be used to identify PFOA branched isomers and to include them with the linear isomer to provide a total PFOA sample concentration.

NOTE 1—Draft Method 1633 adds qualitative branched isomer standards for 6 additional PFAS. That makes a total of 11 PFAS out of 40 target compounds that can be reported as total linear and branched - 4 using the quantitative standard and 7 using the qualitative standard for isomer identification. For the remaining target compounds, only the linear isomer is quantified. As other quantitative standards that include the branched isomeric PFAS forms become available, they should be incorporated into the applicable PFAS analytical methodologies, which will allow for the total (and separately branched) PFAS concentration to be determined for these analytes.

5.10 *Data Reporting Format:*

5.10.1 Laboratory data reporting formats should be considered during the project planning process and documented in the project QAPP. Data reporting format decisions should consider the range of data uses for the project application. Data uses may include site characterization, site remediation, source control, treatment of effluent, treatment of drinking water, risk assessment, and regulatory compliance monitoring. Data management decisions should consider the full range of intended data uses and should be reviewed by the laboratory and documented in the project QAPP.

5.10.2 Laboratory data reports typically include a set of standardized elements as listed below:

(1) Cover sheet

(2) Table of contents

(3) Case narrative

(4) Chain-of-custody records

(5) Sample receipt documentation

(6) Data report (Form 1s)

(7) QC documentation (detail depends on reporting level)

(8) Sample preparation logs (included in Level IV data package)

(9) Raw data for each sample, blank, spike, duplicate, and standard (that is, quantitation reports, chromatograms, mass spectra, instrument printouts, and bench sheets) (included in Level IV data package)

5.10.3 Data package deliverables produced by laboratories contain various levels of detail and are typically categorized into the levels listed below:

(1) Level IV—Comprehensive validation-ready fully documented data package inclusive of raw data

(2) Level III—Summary data with calibration and QC forms, excludes raw data

(3) Level II—Summary data with QC forms, excludes raw data

(4) Level I—Results-only data report, excludes QC forms and raw data

5.10.4 Project planning should also consider the electronic data deliverables (EDD) format(s) needed to support project data uses. EDD formats typically produced by environmental laboratories include CSV, Excel, and commercially available enterprise database file formats. These may be unformatted or formatted to conform to a practitioner's specific database. State regulatory programs may require a formatted EDD for a specific program application. Examples include, but are far from limited to, the New Jersey Hazsite EDD designed for upload to the New Jersey Department of Environmental Protection (NJDEP) Site Remediation Program database, and the New Jersey Electronic Environmental (E2) Reporting System EDD designed for upload to the database for the Safe Drinking Water Act (SDWA) compliance monitoring program administered by the NJDEP Bureau of Safe Drinking Water. Federal programs may require a formatted EDD for a program-specific data application. Examples include the Environmental Resources Program Information Management System (ERPIMS) EDD used by the U.S. Air Force Civil Engineer Center (AFCEC) for validation and management of data from environmental projects at Air Force bases, and the Staged Electronic Data Deliverable (SEDD) used by the USEPA Superfund program with automated data review tools.

5.11 *Sample Disposition:*

5.11.1 Project planning should also consider the timeline for retention and disposal of samples by the receiving laboratory. These may include unused sample material, sample extracts, sample containers, expired reagents, and related waste generated in the processing of environmental samples. Laboratories typically follow waste management plans, use licensed waste disposal contractors, and maintain records of waste management. Project planning decisions should account for the total time the samples and residuals are retained by the laboratory prior to disposal (or return) relative to the time needed by data users for data review and evaluation. Laboratories must be notified regarding projects with Consent Orders and Legal Hold requirements that stipulate indefinite storage of samples and residuals. Effective communications must take place between practitioners and the laboratory to secure capacity and funding for long-term storage of unused samples, sample extracts, and residuals.

6. Analytical Method Selection Considerations

6.1 *Overview:*

6.1.1 The ongoing, expanding nature of PFAS environmental awareness and the need for more comprehensive investigations have caused increased demand for PFAS environmental sampling and analysis. There are limited analytical method options available, particularly across the full spectrum of environmental media for a range of PFAS compounds. In many cases, the primary source in the search for available analytical methods for any environmental application is the USEPA. The USEPA has published analytical methods for the analysis of select PFAS analytes in drinking water and non-potable water, and USEPA released a draft method for the analysis of select PFAS analytes in nonpotable water, soil, sediment, biosolids, and tissue. In addition to the USEPA, both the ASTM and the International Organization for Standardization (ISO) have also published PFAS analytical methods. These methods are discussed in Section 7.

6.2 *Interplay of Sampling Objectives and Regulatory Requirements:*

6.2.1 PFAS sampling and analytical programs are no different than other environmental sampling programs in that the procedures used must comply with applicable regulatory requirements. As discussed in 5.4, the PFAS regulatory framework is rapidly evolving. This, in combination with the limited availability of PFAS analytical methods, makes the development of project SAPs for PFAS much more challenging relative to other environmental sampling programs. Practitioners and data users must continually check for revisions to the applicable regulatory requirements between writing the plan and executing it.

6.2.2 Another major consideration is that, given the limited number of standardized, published, multi-laboratory validated analytical methods to determine a wide range of PFAS in a wide range of sample matrices, practitioners may have no other option except to use a laboratory-specific, proprietary method. This is commonly the case when there are specific PFAS that need to be included and a published method for those compounds is not available. More prevalent are cases where environmental media such as soil, sediment, or biologic tissue need to be analyzed for a specific list of PFAS target analytes using a robust analytical approach to accommodate sample matrix effects for which published analytical methods do not exist. Proper planning is essential for any environmental data acquisition program. For projects that include PFAS, comprehensive planning with the involvement of all data users and the laboratory is paramount and quite literally can be the difference between success and failure.

6.2.3 PFAS environmental investigations should be conducted in compliance with applicable regulatory requirements. Regulations at the national level, such as the SDWA, and protocols, such as the U.S. Department of Defense (DoD) Quality Systems Manual (QSM) (1)[5], may differ from or conflict with state, regional, or provincial regulatory requirements. In many cases, these jurisdictional regulatory conflicts add a confounding degree of complexity.

6.2.4 The analysis of public water supplies in the United States is regulated under the SDWA. The USEPA released Method 537 for PFAS in 2009, with revision in 2018 as Method 537.1, revised in 2020. The USEPA also released Method 533 for drinking water analysis in 2019.

6.2.5 The DoD manages all environmental analysis in accordance with their QSM. PFAS contamination has varying degrees of concern at DoD sites, and that concern may not be limited to public water supplies. DoD environmental sampling programs often include additional PFAS and other environmental media that are not addressed by existing USEPA methods. Because of this, laboratory-specific, proprietary PFAS analytical methods are often used. To manage the application of these methods and to standardize wherever possible, the DoD QSM established method performance and QA/QC requirements. The DoD QSM represents a logical first step toward the standardization of PFAS analytical methods, particularly those that include additional compounds or address other environmental media until additional recognized standard methods are promulgated.

6.2.6 The partnership between the USEPA and the DoD Strategic Environmental Research and Development Program (SERDP) has produced draft Method 1633 (August 2021, rev. June 2022, rev. Dec. 2022, rev. July 2023) for determination of 40 PFAS target analytes in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. This draft method can be used in various applications, including National Pollutant Discharge Elimination System (NPDES) permits. The method will support NPDES implementation by providing a consistent PFAS method that has been tested in a wide variety of wastewaters and contains all the required quality control procedures for a Clean Water Act (CWA) method. This method can also be used for DoD applications. The DoD QSM Ver. 5.4 (released in October 2021) included in Appendix B Quality Control Requirements, the Table B-24 for PFAS Draft Method 1633.

6.2.7 As a screening option, the USEPA released draft Method 1621 in April 2022 for the analysis of Adsorbable Organic Fluorine (AOF). This method-defined parameter can be used for the measurement of organofluorines that adsorb onto carbon sorption media for wastewater and surface water sample analysis applications. The method limitations are higher detection limit, potential for low recoveries of short chained PFAS, potential for matrix interferences (such as total suspended solids, other organic co-contaminants, inorganic fluoride), and non-applicability to solid sample matrices.

6.3 *Source Identification, Site Characterization, and Remedial Design Applications:*

6.3.1 Many of the concepts and principals that apply to conducting routine environmental site assessments also apply to PFAS sites. Generally speaking, the intent is to identify the source(s) of contaminants as well as the nature and extent of the contamination. A conceptual site model is developed, and a SAP is prepared to either confirm or further elucidate the sources, pathways, and receptors addressed in the conceptual site model. SAPs can be application specific in that the targeted PFAS list could vary depending on whether the data collection activity is strictly for regulatory compliance or the information is also being used for remedial design or source identification. PFAS adds a degree of complexity due to the rapidly developing regulatory framework, the limited availability of standardized PFAS analytical methods, and the limited availability of internal, isotopically labeled standards.

6.4 *Non-Targeted Analysis—Tools for the Forensic Practitioner:*

6.4.1 When analyzing samples for environmental contaminants, the usual quest is to accurately quantify a relatively short list of targeted compounds and trace elements. Mass spectrometry (MS) environmental methods focus on the USEPA Target Compound List or a project-specific list of contaminants of concern, capturing only those compounds with established cleanup benchmarks. These analyses cover only perhaps 200–300 of the 65 million chemicals identified in the CAS database.

6.4.2 PFAS include a wide variety of head groups, chain lengths, and branching, so thousands of such chemicals may be present in the environment. However, because regulatory analytical methods are targeted, the MS data are typically acquired in a filtered mode (for example, multiple reaction or transition monitoring), such that only specific analyte types can be "seen." This severely limits the ability for practitioners to distinguish among types and sources of contamination.

6.4.3 With the advent of high-resolution tandem (and hybrid) MS instrumentation and chemical informatics software, practitioners have access to new tools to strengthen and broaden the application of non-targeted analysis (NTA) techniques. Using these tools, much more chemical information can be extracted from the same samples, enabling rapid characterization of thousands of chemicals in environmental media and the chemical sources.

6.4.4 In 2017, a team of researchers from Oregon State University, the Colorado School of Mines, Duke University, and the University of Guelph used a tandem MS set up to capture "all" of the MS data and found 40 previously unreported classes of PFAS present in samples impacted by aqueous film-forming foams (AFFFs) (2). The Society of Environmental Toxicology and Chemistry (SETAC) has recognized the expansive data collection needed to assess risk for the growing list of PFAS. SETAC held special conferences in 2019 and 2020 that focused solely on NTA for environmental assessment. At the 2020 North American Meeting of SETAC in Toronto, Ontario, there were more than 50 presentations on NTA—most of which were focused on PFAS.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

6.4.5 The USEPA has recognized the importance of NTA and has launched the Non-Targeted Analysis Collaborative Trial (ENTACT). ENTACT is designed to determine how measurement data generated from NTA methods can be used to direct high-throughput screening (HTS) research and strengthen chemical safety evaluations, and to demonstrate how resources procured for HTS research in support of chemical safety evaluations can be used to advance NTA methods. ENTACT is applying USEPA's ToxCast library of approximately 4 000 compounds and is conducting studies to identify the most accurate NTA methods and workflows. ENTACT involves more than 25 government, academic, and private/vendor laboratories internationally. For more information refer to: Sobus, J.R., Wambaugh, J.F., Isaacs, K.K. et al. Integrating tools for non-targeted analysis research and chemical safety evaluations at the USEPA. Journal of Exposure Science and Environmental Epidemiology 28, 411–426 (2018). https://doi.org/10.1038/s41370-017-0012-y.

6.4.6 With the addition and growing availability of high-resolution LC/MS/MS instruments in commercial laboratories, there is greater opportunity to broaden the application of these non-target identification techniques for PFAS and other analyte groups.

6.4.7 Researchers from the University of Washington (Tacoma and Seattle) and the Center for Urban Waters (Tacoma) have demonstrated using high mass resolution LC/MS/MS data in an analytical and data reduction technique to estimate source contributions based on NTA data. They report, "Relying solely on the richness of this data and avoiding the need for individual targeted contaminants, we developed a novel method to quantitatively estimate chemical source contributions to complex mixed systems that generated accurate estimates … even in multisource systems with < 1% source contributions" (**3**).

6.4.8 Using file import techniques, practitioners can import routine PFAS instrument files from commercial laboratories to assess isomer patterns of targeted PFAS homologs. To obtain functional import files, it is important to work with laboratory providers to coordinate the instrument acquisition parameters needed for NTA. With accessible PFAS instrument files, practitioners can use a variety of software tools and workflows to visualize and perform MS/MS interpretation and library searches. It can be of great value to capture all data for suspected sources when sampling to perform nature and extent studies. This can be as simple as having the laboratory run a second analysis in a "data independent" mode and archiving the file or conducting an NTA screen to determine whether evidence for multiple sources can be identified.

7. Analytical Methods Comparison

7.1 This section provides a summary of the available published PFAS analytical methods. Table 1 outlines the basic requirements of each method. Table 2 compares the respective target compound lists determined by each method.

7.2 *USEPA Drinking Water Methods:*

7.2.1 USEPA released Method 537 in 2009 for determination of 14 PFAS target analytes in drinking water. Method 537 was revised in 2018, designated as Method 537.1, with the addition of 4 PFAS target analytes for a total of 18 target analytes. USEPA released Method 533 in 2019 for determination of 25 PFAS target analytes in drinking water. Although there is a lot of overlap between the Method 537.1 and the longer Method 533 compound lists, not all of the 18 Method 537.1 compounds are listed under Method 533. A maximum of 29 PFAS can be determined in drinking water by performing both Method 537.1 and Method 533. Method 533 differs from Method 537 and Method 537.1 in that it incorporates an isotopic dilution approach using extracted internal standards as part of its calibration requirements, it uses a different SPE cartridge, and it uses a different sample preservation technique.

7.3 *Other USEPA PFAS Analytical Methods:*

7.3.1 USEPA Office of Solid Waste released Method 8327 in draft in June 2019 and as final in July 2021. This USEPA method is applicable to non-potable aqueous sample media such as groundwater, surface water and wastewater. This direct injection method incorporates a methanol–water cosolvation followed by filtration rather than an SPE sample introduction approach and utilizes an external calibration procedure. The method , validated for 24 target analytes, notes, "The Statistical Report and Data Validation Summary showed more bias and/or less robust measurement precision for the longer-chain carboxylic acids, the amidoacetic acids, the fluorotelomer sulfonic acids, and perfluorobutanoic acid."

7.3.2 USEPA Office of Water released draft Method 1633 the first draft in September 2021, second draft in June 2022, third draft in December 2022, and fourth draft in July 2023 for analysis of 40 target PFAS analytes in non-potable water, soil, sediment, biosolids, and biological tissue samples. This method incorporates an isotopic dilution approach using extracted internal standards as part of its calibration requirements, with sample extraction using an SPE cartridge, and different sample preparation and cleanup techniques for each sample matrix type. This performance-based method, with additional flexibility described at 40 CFR 136.6, was developed for Clean Water Act applications. This draft method underwent a single-laboratory validation in 2021 and a multi-laboratory method validation study in 2022. The multi-laboratory validation study report for the aqueous (wastewater, surface water, and groundwater) sample matrices for draft 1633 method was released in July 2023.

7.3.3 USEPA Office of Water released Draft Method 1621 in April 2022 for Screening Method for the Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC). This single laboratory validated method can be used to screen for the presence of soluble organofluorines in wastewater. The limitations of this screening method include *(a)* it does not identify which organofluorines are present, *(b)* it does not quantify all organofluorines (for example, insoluble fluoropolymers), and *(c)* it has some known interferences that are discussed the method. A multi-laboratory validation study of this method is underway; the study results will be used to finalize the method and add formal performance criteria.

7.4 *ASTM PFAS Analytical Standards:*

7.4.1 ASTM released Test Method D7968 in September 2014 and Test Method D7979 in February 2015 and Test Method D8421 in November 2021.

TABLE 1 Published PFAS Analytical Methods: Methodology Overview and Comparison

Comparison	Method Author									
	USEPA ORD	USEPA ORD	USEPA Office of Water	USEPA Office of Solid Waste	USEPA Office of Water	ASTM	ASTM	ASTM	ISO	ISO
Method	537	537.1	533	8327	1633	D8421	D7968	D7979	25101	21675
Version	1.1	2.0	0	0 (2021)	Fourth Draft	2021	-2017	-2020	-2009	-2019
Year First Published	2009	2020	2019	2019	2021	2021	2014	2015	2009	2019
Sample Media	DW	DW	DW	Non-DW: GW, SW, WW	Non-DW: GW, SW, WW; Solid: Soil, Sediment, Biosolids, Tissue	Non-DW: GW, SW, WW	Soil /Sediment, Sludge, Waste	Non-DW: GW, SW, WW	DW, GW, SW, WW	DW, SW, WW
Compounds Determined	14	18	25	24	40	44	31	31	2 (focus on linear isomers)	30 (focus on linear isomers)
Preservative	Tris buffer	Tris buffer	Ammonium acetate	none	none	none	none	none	Dechlorinating agent	Dechlorinating agent
Temperature	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C	4 < or = 10 °C
Hold Time (Extract / Analyze)	14 / 28 days	14 / 28 days	28 / 28 days	28 / 30 days	28 / 28 days (HT varies based on sample storage temperature, and target analytes)	28 days	28 days	28 days	14 days	28 days
Sample Preparation	SPE cartridge (SDVB)	SPE cartridge (SDVB)	SPE cartridge (SDVB) with a positively charged diamino ligand (weak anion exchange)	Entire sample processed in original container, spiked with surrogates, add MeOH, mix, filter, adjust pH, then direct aqueous injection	SPE cartridge (WAX)	Entire sample processed in original container, spiked with surrogates, add MeOH, mix, filter, adjust pH	Spike with surrogates, tumble with MeOH:H_2O, centrifuge, extract, filter, adjust pH	Entire sample processed in original container, spiked with surrogates, add MeOH, mix, filter, adjust pH	SPE	SPE, weak anion exchange
Instrument	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS
Calibration	Internal standard (3)	Internal standard (3)	Internal standard (3)	External standard	Internal standards (24) (isotope dilution)	External standards (24) (isotope dilution optional)	External standards	External standards (isotope dilution optional)	Internal standards (2)	Internal (18) or external standards
Analyte Quantitation	Internal standard (non-isotope dilution)	Internal standard (non-isotope dilution)	Internal standard (isotope dilution)	External standard (non-isotope dilution)	Internal standard (isotope dilution)	External standard (isotope dilution optional)	External standard (non-isotope dilution)	External standard (isotope dilution optional)	Internal standard (isotope dilution)	Internal standard (isotope dilution) or external standard