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CP2-ES-2000/FR1

Per- and Polyfluoroalkyl Substances Analyses Data Verification and Validation for the Paducah Gaseous Diffusion Plant, Paducah, Kentucky

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Per- and Polyfluoroalkyl Substances Analyses Data Verification and Validation for the Paducah Gaseous Diffusion Plant Paducah, Kentucky

Date Issued—December 2025

U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

Prepared by
FOUR RIVERS NUCLEAR PARTNERSHIP, LLC,
managing the
Deactivation and Remediation Project at the
Paducah Gaseous Diffusion Plant
under Contract DE-EM0004895

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APPROVALS

Per- and Polyfluoroalkyl Substances Analysis
Data Verification and Validation for the
Paducah Gaseous Diffusion Plant
Paducah, Kentucky

CP2-ES-2000/FR1

December 2025

Approved by:

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REVISION/CHANGE LOG				
Revision/ Change Letter	**Description of Changes**	**Pages Affected**	**Date of Revision/ Change**	**Approved By (signature on file)**
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FR1	General revision to update plan according to DoD/DOE QSM 6.0 requirements to address CA-005369, AI-0008630.	All	12/18/2025	Signature on file

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CONTENTS

TABLES

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ACRONYMS

%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
%RSE	percent relative standard error
CCV	continuing calibration verification
COC	chain-of-custody
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
IAR	ion area ratio
IB	instrument blank
ICV	initial calibration verification
ISC	instrument sensitivity check
LC/MS/MS	liquid chromatography/tandem mass spectrometry
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
N/A	not applicable
PFAS	per- and polyfluoroalkyl substances
QAPP	quality assurance project plan
QC	quality control
RF	response factor
RL	reporting limit
RPD	relative percent difference
RR	relative response
RT	retention time
SAEP	sampling analysis and event plan
SAP	sampling and analysis plan
SDG	sample delivery group
SMO	sample management office
S/N	signal-to-noise ratio
SOW	statement of work
SQL	sample quantitation limit

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DEFINITIONS

NOTE 1: Data validation code definitions are listed in Appendix A.

NOTE 2: In this plan, the words "shall" and "must" are used to denote a requirement; the word "should" be used to denote a recommendation; and the word "may" is used to denote permission (neither a requirement nor a recommendation). In conformance to this plan, all steps shall be performed in accordance with its requirements, but not necessarily with its recommendations; however, justification must be documented for deviations from recommendations.

Affected Sample Result—A sample result is considered affected when the result is significantly influenced by a quality deficiency and is qualified accordingly through analytical data validation.

Batch—A group of samples prepared at the same time in the same location using the same method, not to exceed 20 samples of similar matrix.

Case—A finite, usually predetermined number of samples, that has been collected over a given time period from a particular site. A case consists of one or more sample delivery groups.

Chain-of-Custody—The history of the transfer of samples from the time of sample acquisition through archival and disposal of samples. Chain-of-custody documentation is required as evidence of sample integrity.

Confirmation Ion—Produced by collisional activated dissociation of a precursor ion to produce distinctive ions of smaller mass to charge than the precursor.

Continuing Calibration Verification—A standard solution analyzed at a specified frequency during an analytical run to assure continued validity of the calibration curve.

Correctable Problem—Correctable problems are deficiencies within data packages that may be rectified through consultation with the laboratory. Correctable problems may be revealed during both data verification and data validation. Correctable problems that are revealed during verification are those deficiencies that can be addressed by obtaining additional information from the laboratory. Correctable problems that are revealed during validation are those deficiencies with analyses that can be solved either by a second preparation and/or by analysis of a sample.

Data Quality Objective—Data quality objectives are qualitative and quantitative statements derived from the outputs of each step of the data quality objective process that specify the study objectives, domain, limitations, the most appropriate type of data to collect, and also specify the levels of decision error that will be acceptable for the decision.

Data Quality Objectives Process—The data quality objective process is a quality management tool based on the scientific method and developed by the U.S. Environmental Protection Agency to facilitate the planning of environmental data collection activities. The data quality objective process enables planners to focus their planning efforts by specifying the use of the data (the decision), the decision criteria (action level), and the decision maker's acceptable decision error rates.

Data Validation—Data validation is a systematic process that is performed independently from the data generator, which applies a defined set of performance-based criteria to a body of data that may result in physical qualification of the data. Data validation occurs prior to drawing a conclusion from the body of data.

Data Verification—Data verification is a systematic process of evaluating the completeness, correctness, consistency, and compliance of a set of facts against a standard or contract that is performed either by the data generator or by an entity independent to the data generator.

Holding Time—Holding time, as described in this plan, is defined as the period of time between sample collection and sample activity determination.

Initial Calibration—Initial calibration, as described in this plan, is defined as the standardization of a gas chromatography instrument against a traceable standard of known identity and quantity. This standardization prevails until such a time that analytical conditions are deemed out of acceptable control limits.

Internal Standard—Labeled compound spikes or nonextracted recovery standards, and they are added to every per- and polyfluoroalkyl substances standard, blank, matrix spike, duplicate, and sample extract at a known concentration, prior to instrumental analysis. Internal standards are used as the basis for quantitation of the isotopically labeled compounds. Internal standards can also be called nonextracted internal standards.

Isotope Dilution Quantitation—A means of determining a native compound by reference to the same compound in which one or more atoms has been isotopically enriched. The labeled per- and polyfluoroalkyl substances are spiked into each sample and allow identification and correction of the concentration of the native compounds in the analytical process.

Isotope Dilution Standard—An analog of a target analyte in the method which has been synthesized with one or more atoms in the structure replaced by a stable (nonradioactive) isotope of that atom. Common stable isotopes used are carbon-13 or deuterium. These labeled compounds do not occur in nature, so they can be used for isotope dilution quantification or other method-specific purposes. Isotope dilution standards can also be called extracted internal standards. The external internal standards are added to the sample at the beginning of the sample preparation process and are used to quantify the native target analytes.

Laboratory Control Sample—The laboratory control sample is a control sample of a known composition. Aqueous and solid laboratory control samples are analyzed using the same preparation, reagents, and method employed for field samples.

Laboratory Duplicate—The laboratory duplicate is a randomly chosen split of an analytical sample into two aliquots prior to sample preparation. The purpose of a laboratory duplicate is to monitor the precision of the analytical method.

Matrix Spike—The matrix spike is a split of a field-originating analytical sample in which one half of the split is spiked with a known amount of radionuclide of interest prior to sample preparation. The purpose of a matrix spike is to measure the effect of interferences from the sample matrix that will preclude accurate quantitation by the instrumentation.

Method Blank—The method blank is a laboratory-generated sample of the same matrix as the analytical samples, but in absence of the analyte of interest. The purpose of a method blank is to monitor the presence of contamination of the analyte of interest in the sample preparation and analysis processes.

Method Detection Limit—The method detection limit is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

Noncorrectable Problem—Noncorrectable problems are deficiencies within a data package that preclude the evaluation of data quality by predefined criteria. Noncorrectable problems may be revealed during both data verification and data validation.

Per- and Polyfluoroalkyl Substances—A group of man-made fluorinated compounds that are hydrophobic and lipophobic, manufactured and used in a variety of industries globally. These compounds are persistent in the environment as well as in the human body.

Practical Quantitation Limit—The practical quantitation limit is defined as the lowest concentration of a contaminant that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation limit is typically several times higher than the method detection limit.

Preparation Batch—A preparation batch is a group of sample aliquots prepared together at the same time using the same method and related to the same quality control samples.

Relative Percent Difference—Relative percent difference is the measure of precision between two values, defined as the absolute value of the difference between two values divided by the mean of the two values.

Relative Standard Difference—Relative standard deviation is the measure of precision between multiple values, defined as the standard deviation of multiple values divided by the mean of the values.

Reporting Limit—The reporting limit is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

Required Detection Limit—The required detection limit is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

Sample Delivery Group—A sample delivery group is defined by one of the following, whichever occurs first: (1) case of field samples; (2) each 20 field samples within a case; (3) each 14-day calendar period during which field samples in a case are received, beginning with receipt of the first sample in the sample delivery group.

Sample Quantitation Limit—Sample quantitation limits are detection limits based on the required detection limit, which have been modified due to deviations from analytical method specifications, such as sample weight and extract volume or due to dilution or percent moisture.

Sample Result—A sample result, as described in this plan, is a numeric denotation of the concentration, amount, or activity of a specific analytical parameter uniquely associated with an aliquot of environmental media.

Signal-to-Noise Ratio—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the mean height of the noise.

Surrogate—Nontarget standard compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard used to evaluate analytical efficiency by measuring percent recovery. Surrogates are not expected to be present in environmental media.

Turnaround Time—Contractually specified as the amount of time that elapses between laboratory receipt of the raw samples and subsequent data receipt by the client.

Validation Code—A validation code is an alphabetic character physically or electronically associated with a discrete sample result during validation due to a data quality deficiency, which provides guidance in data usability.

Validation Statement of Work—The validation statement of work is a document prepared to function as the mechanism by which validation implementation requirements are communicated from the sample management office to the validation organization.

1. INTRODUCTION

1.1 PURPOSE AND SCOPE

This plan provides guidance for the verification and validation of per- and polyfluoroalkyl substances (PFAS) analysis laboratory data performed by an external party. For the purpose of this guidance, external parties are defined as organizations (including governmental entities, contractors, or vendors) that conduct analytical data review, verification, and validation activities, and that are not part of the immediate laboratory that generates the subject analytical data (but are part of the overall project-specific data review process).

This document focuses on data generated by liquid chromatography/tandem mass spectrometry (LC/MS/MS) for PFAS using U.S. Environmental Protection Agency (EPA) Method 537.1, *Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)* and Method 1633A, *Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS* (EPA 2020). When applicable, this plan incorporates requirements that are defined in the *Department of Defense and U.S. Department of Energy Quality Systems Manual for Environmental Laboratories Version 6.0* (DoD/DOE QSM); however, data validators should reference the most current version of the DoD/DOE QSM when validating data (DoD and DOE 2023). Data produced by analytical methods for which this plan provides limited guidance (i.e., SW-846 Method 8327) may necessitate the development of modified criteria from this plan; however, the general validation strategy outlined in this plan should be applicable (EPA 2021). In the absence of specific guidance, data validators are advised to seek guidance in the specific method employed and/or from other industry standards. Examples include the National Functional Guidelines for Organic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

1.2 APPLICABILITY

Data verification and validation is a systematic process, which is performed externally from the data generator that applies a defined set of performance-based criteria to a body of data that can result in the application of validation codes to the data. The project team, with input as needed from a quality assurance specialist and/or representative of the sample management office (SMO), shall develop a data validation strategy based on inputs identified through the data quality objective (DQO) process. The project-specific sampling and analysis plan (SAP), sampling analysis and event plan (SAEP), or quality assurance project plan (QAPP) will define the DQOs and framework for performing data validation.

Data verification is the process of checking data for completeness, correctness, consistency, and contract compliance. These requirements are contained in the analytical laboratory statement of work (SOW) and/or project-specific planning documents (e.g., SAP, SAEP, QAPP). The data verification process compares the laboratory data package to requirements associated with the project. The data verification process can identify deficiencies in the laboratory data package that can be addressed by obtaining additional information from the laboratory.

Data validation is the process of examining a laboratory data package to provide a level of confidence in the reported analyte's identification, concentration (including detectability), and associated measurement uncertainty. The data validation process begins with a review of the laboratory data package to screen the areas of strength and weakness of the data. The data validation process continues with assessing the data against standardized procedures and criteria to confirm the presence or absence of an analyte and to evaluate the uncertainty of the quantification for the analyte. Each data point is then qualified as to its integrity and dependability in the context of the project requirements based on all available laboratory data.

2. RESPONSIBILITIES

Table 1 summarizes the responsibilities of data validator and the SMO.

Table 1. Responsibilities for Data Validator and SMO

Performer	Responsibilities
Data Validator	• Determines if all required information is presented in the laboratory data package. • Makes objective judgments and decisions about the data quality and defensibility. • Assigns data validation codes to the results. The data validation codes indicate the validity and usability of the data and the limitations on its end use. • Produces a data validation report.
SMO	• Reviews each data validation report. • Adds data validation codes to data in the project environmental measurements system. • Distributes the data validation report to the appropriate personnel.

3. GENERAL INFORMATION

3.1 LEVELS OF LABORATORY DATA DELIVERABLES

Laboratory data deliverables consist of a combination of forms and raw data. Depending upon the required laboratory report elements included, the deliverable can range from Level I to a Level IV laboratory data package. Level IV laboratory data packages are typically used for data validation purposes. The elements included in a laboratory data package for each level are provided in Table 2.

Table 2. Required Laboratory Report Elements

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
Cover/Signature Page/Executive Summary	✓	✓	✓	✓
Table of Contents	✓	✓	✓	✓
Laboratory Report Narrative	✓	✓	✓	✓
Method Summary		✓	✓	✓
Sample Summary/Sample Data Sheets	✓	✓	✓	✓
Shipping and Receiving Documents	✓	✓	✓	✓
Client Chain-of-Custody (COC)	✓	✓	✓	✓
Sample Receipt Checklist	✓	✓	✓	✓
Interlab COC (where applicable)	✓	✓	✓	✓

Table 2. Required Laboratory Report Elements (Continued)

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
Subcontract Laboratory COC (if required)	✓	✓	✓	✓
Glossary of Abbreviations and Laboratory Definitions	✓	✓	✓	✓
Quality Control (QC) Association Summary/Sample Traceability	✓	✓	✓	✓
Analysis Run Log			✓	✓
Surrogate and/or Tracer and Carrier Recovery Report	✓	✓	✓	✓
Method Blank (MB) Reports		✓	✓	✓
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD) Summary		✓	✓	✓
Matrix Spike (MS)/Matrix Spike Duplicate (MSD) Summary		✓	✓	✓
Duplicate Sample Summary		✓	✓	✓
Instrument Performance Check Summary			✓	✓
Calibration Data			✓	✓
Internal Standard Area and Retention Time (RT) Summary			✓	✓
Continuing Calibration [Initial Calibration Verification (ICV)/Continuing Calibration Verification (CCV)] Summary Report			✓	✓
Instrument Blank Report			✓	✓
Detection Limits Summary			✓	✓
GC Dual Column Identification Summary			✓	✓
Linear Ranges			✓	✓
Preparation Batch Log			✓	✓
Interference Check Standard Summary			✓	✓
Serial Dilution Summary			✓	✓
Cleanup Log			✓	✓
Standard/Reagent Traceability Log			✓	✓
Accreditation/Certification Summary			✓	✓
Raw Sample Data			✓	✓
Raw QC Data			✓	✓
Manual Integration Summary			✓	✓

*Report elements listed represent common elements. The laboratory may provide more or less information as required by the method being analyzed. For example, those wet chemistry methods with no true calibration information will not have calibration forms included in the laboratory data package.

3.2 STAGES OF VALIDATION

For the purposes of this plan, the following terminology is recommended for use to describe the stages (extent) and processes that are used to validate laboratory analytical data packages, whether the validation is performed by a manual process, electronic process, or combination of both.

NOTE: The following lists of required activities per each stage of validation is not considered an "all-inclusive" list or applicable to every method that is validated.

- **Stage 1 Validation**: A verification and validation based only on completeness and compliance of sample receipt condition checks. Client sample IDs and target analytes are verified against the COCs for completeness; sample conditions upon arrival at laboratory noted; sample preservation was appropriate and verified by the laboratory; holding times were met; concentrations and units were

aappropriate; trip blanks, field blanks, and equipment blanks, and field duplicates met the project requirements for frequency and field QC.

- **Stage 2A Validation**: A verification and validation based on completeness and compliance checks of sample receipt conditions and **ONLY** sample-related QC results. MBs, LCSs, MSs, laboratory duplicates (including LCSD and MSD), surrogates (organics), serial dilutions, post-digestion spikes (as appropriate to the method) and any preparatory batch cleanup QC to assure that project requirements for analyte spike list, frequency, and QC limits are met.

- **Stage 2B Validation**: A verification and validation based on completeness and compliance checks of sample receipt conditions and **BOTH** sample-related and instrument-related QC results.

- **Stage 3 Validation**: A verification and validation based on completeness and compliance checks of sample receipt conditions, both sample-related and instrument-related QC results, **AND** recalculation checks.

- **Stage 4 Validation**: A verification and validation based on completeness and compliance of sample receipt conditions, both sample-related and instrument-related QC, recalculation checks **AND** the review of actual instrument outputs.

The stage of validation required is generally defined at the program or project level. Validation parameters to be reviewed depending on the stage of validation can include instrument calibrations, calibration verification checks, QC sample results, analytical yields, holding times, and sample preservation. It is not the role of data validation to determine if project goals are met or to provide the decisions to be made. Data validation provides the overall appraisal of a data set and the project team should use this appraisal along with their own judgment to make their own decisions.

3.3 DATA ASSESSMENT REVIEW

The data assessment review includes the following.

- Data verification/contractual screen
- Data validation (if requested)
- Data assessment
- Data usability assessment

The data assessment review is comparable to a Stage 1 and Stage 2A validation (depending on analyte and method). As required by project-specific requirements, a Stage 2B, Stage 3, or a Stage 4 validation of the data package **MAY** be requested. See CP3-ES-5003, *Quality Assured Data*, for more information about the data assessment review process.

3.3.1 Data Verification/Contractual Screen

Data verification is the first step of the data assessment review process. The preferred method for performing verification is electronic. Verification criteria are documented using CP3-ES-5003-F01, "Data Assessment Review Checklist and Comment Form," and CP3-ES-5003-F05, "Data Verification/Validation Checklist" (if Stage 2B, Stage 3, or Stage 4 data validation is required). Data verification is performed on 100% of data.

3.3.2 Data Validation

Data validation (if requested) follows data verification in the data assessment review process when requested by the project team. Stage 3 and Stage 4 validations must be performed by a third party. Third-party data validation is defined as validation that is performed by persons independent from the sampling, laboratory, and decision making for the project (i.e., not the project reviewer). Data validation is documented in a formal deliverable from the data validator. The stage and frequency that are chosen for validation is based on project requirements and the following considerations.

- Regulatory drivers/requirements
- End-user of data
- Future applicability of the data (other users such as regulatory agencies, risk assessment personnel, internal users, etc.)
- Legal ramifications and defensibility of data
- Confidence in laboratory (DOE Consolidated Audit Program-approved laboratory)

The project team determines if the data set requires validation. The project team also determines the stage and frequency of data validation.

When data validation is requested by the project, a validation SOW is prepared by the SMO to communicate data verification and validation requirements to the external party performing the data validation. Along with the validation SOW, full copies of the laboratory data packages, as well as an electronic data deliverable in the form of a Microsoft Excel file are sent to the data validators performing the validation. CP3-ES-5003-F05 is provided to the validator from the SMO and must be completed for every laboratory sample delivery group (SDG) being validated.

3.3.3 Data Assessment

Data assessment follows data verification and data validation (if requested) in the data assessment review process. Data assessment is performed by data reviewers who have been trained to evaluate laboratory quality assurance/QC requirements. Data assessment is performed on 100% of data.

3.3.4 Data Usability Assessment

Data usability assessment is the last review step of the data assessment review process prior to release of the data from the project team. Data usability assessment is an integration of all information collected about a result. Data verification and validation can ensure that analyses are correct; however, data usability assessment must be performed to evaluate the data usability. This includes a review of the data itself, the results of all previous reviews of the data, checking data for trends, and an evaluation against the intended purpose for data collected. Data usability assessment must be performed for all data collection activities and documented using CP3-ES-5003-F01. Data usability assessment is required prior to use of the data, or data release into the final data repository (i.e., Oak Ridge Environmental Information System). Data usability assessment is performed on 100% of data.

4. DATA VERIFICATION AND VALIDATION INSTRUCTIONS

NOTE 1: Data verifier and data validator may be the same individual. CP3-ES-5003-F05 is only completed for Stage 2B, Stage 3, and Stage 4 validations. Appendix B has qualification tables for multiple quality deficiencies.

NOTE 2: **If** data reviewers use this plan as a guide for qualifying data during data assessment, **then** they should apply equivalent data assessment codes in place of the data validation codes referenced in this plan.

4.1 SAMPLE RECEIPT CONDITIONS

4.1.1 Chain-of-Custody

The COC form provides the basis for the traceability of project samples, by documenting the sample from its origin through all steps of the sampling, sample handling, and analysis process. The COC serves as documentation of the sample possession from collection through disposal to ensure that sample representativeness is maintained prior to analysis. By documenting personal accountability for samples, the COC is used to ensure that proper custody has been maintained from the time a sample is generated through its final disposition (cradle to grave). Any break in custody, as demonstrated by the series of signatures denoting sample holders, could jeopardize the legal and/or technical defensibility of associated sample data.

While data verification/validation cannot replicate the custody history of a sample (i.e., fully assure that the sample truly has been in custody from the field to the final result), an evaluation of field notes from sample data forms, laboratory records, and the COCs provide the best available indicator of sample traceability. A sample is defined as being under proper custody if any of the following conditions are met:

- The sample is within the possession of an authorized person (e.g., field personnel, laboratory personnel);
- The sample is within view of an authorized person;
- The sample was in an authorized person's possession and then was secured to prevent tampering; or
- The sample is placed in a designated secure area.

NOTE: Verification of sample documentation includes result report header checks for accuracy from the COC. **If** sample identity is in question, **then** every attempt should be made to verify the identity of each sample. When custody problems cannot be resolved, they will affect the defensibility of the sample.

4.1.1.1 Data verification

Trace custody of all samples in the reporting batch from field sampling through receipt at the laboratory by reviewing the COC forms. **If** the information is missing, **then** the data verifier will seek to obtain field documentation from the sampler or laboratory to determine if the omission affects sample integrity. **If** there is a break in the signature chain on the COC, or other omissions in the custody record (e.g., date of sample collection, date of transfer to the laboratory), **then** indicate the problem on the data verification/validation checklist.

4.1.1.2 Data validation

If sample data are not traceable through signature records on COCs, or other sample record information demonstrating custody (e.g., laboratory logbooks and/or sample data forms) cannot establish custody history, **then** the data validator shall apply an "R" validation code to associated results.

4.1.2 Holding Time, Temperature, and Sample Preservation

Holding times have been established by EPA to define the maximum period of time during which a sample remains representative of its sampling location. Holding times begin when a sample is collected in the field and are measured by determining the elapsed time from collection through extraction (when applicable) and/or analysis. **If** the reported data is the result of a dilution, reinjection, or re-extraction and analysis, **then** the result must have been generated within the prescribed holding time in order for the result to be considered definitive.

4.1.2.1 Deliverables

The following are deliverables.

- Sample data forms
- COCs
- Laboratory sample receipt checklist
- Laboratory reports and/or raw data containing the following: dates of collection, preparation, and analysis for all samples, dilutions, and re-extractions

4.1.2.2 Criteria

Table 3 provides current industry-accepted standards for sample preservation and hold times for PFAS parameters. In all cases, the data verifier or validator **shall** always follow the most current methodology guidance for sample holding time, temperature, and preservation requirements.

Table 3. Holding Time and Sample Preservation Criteria

Method	Matrix	Preservatives	Holding Times
537.1	Drinking or Potable Waters	0–10°C preserved with Trizma (once received at laboratory, stored ≤ 6°C prior to extraction)	14 days[a] 28 days[b]
1633A	Aqueous samples (including leachates)	0–6°C and protected from light[c], or frozen ≤ -20°C[d]	28 days[a] 90 days[b,e]
1633A	Solid samples (e.g., soils, sediments)	0–6°C and protected from light[f], or frozen ≤ -20°C[e]	90 days[a] 90 days[b,e]

Table 3. Holding Time and Sample Preservation Criteria (Continued)

[a] Time from collection of sample to extraction.
[b] Time from extraction to analysis.
[c] Conversion of certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids has been observed after 7 days. Specifically, NMeFOSE and NEtFOSE may undergo transformation to NMeFOSAA and NEtFOSAA respectively when stored at 0–6ºC, but not when stored at or below -20ºC; therefore, if NMeFOSE, NEtFOSE, NMeFOSAA, and/or NEtFOSAA are analytes of concern for a given permit or project, either store the samples at or below -20ºC, or extract the samples within 7 days of collection.
[d] When stored at ≤ -20ºC and protected from the light, samples may be held for up to 90 days.
[e] Extracts from all matrix types may be held for up to 90 days if stored in the dark at either 0–6°C, or < -20°C, until analyzed, with the caveat that issues were observed for 11Cl-PF3OUdS and 9Cl-PF3ONS after 28 days. These issues may elevate the observed concentrations of the two ether sulfonates in the extract over time.
[f] Some soils and sediments may exhibit microbial growth when stored at 0–6ºC. Because of its instability, if NFDHA is an important analyte for a given project, samples should be extracted within 3 days of collection.

4.1.2.3 Data verification

Verify the presence of the pertinent COC forms in laboratory data packages. **If** COC forms are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** missing information cannot be obtained or reconstructed from field notes, COC forms, etc., **then** the data verifier will note the omitted information on the data verification/validation checklist as a noncorrectable problem.

4.1.2.4 Data validation

Holding Times

Review the data verification/validation checklist for holding times to confirm all holding times have been met. Holding times that are listed in hours from collection to analysis always will be calculated using the time collected to ensure that the holding time in hours has **NOT** lapsed. Holding times that are listed in days will be calculated using dates only. The data validator **shall** review COC forms, field notes, laboratory report forms, and laboratory raw data, as necessary, to determine the elapsed time from sample collection to sample analysis for deviations identified on the data verification/validation checklist.

If the elapsed time falls within the prescribed holding time, **then NO** action will be taken and **NO** validation code applied.

If the holding time is exceeded, **then** apply validation codes to data as follows.

- **If** the holding time is exceeded by a factor of < 2, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** NFDHA is reported for solid/soil matrix samples **and** was **NOT** extracted within 3 days, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** NMeFOSE, NEtFOSE, NMeFOSAA, and/or NEtFOSAA are reported for aqueous matrix samples **and** were stored at 0–6°C **and** were **NOT** extracted within 7 days, then apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** the holding time is grossly exceeded by a factor of ≥ 2, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

Temperature/ Preservation

Review the laboratory receiving records to determine **if** samples were received at the appropriate temperature. **If** records demonstrate samples were received by the laboratory at the proper temperature, **then NO** action is warranted. **If** temperatures are exceeded, **then** qualify as follows:

- **If** samples are received at elevated temperature, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** samples are collected in unapproved sample containers, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

Table 4 summarizes data validation qualification guidance for samples with holding time exceedances and temperature and/or preservation issues.

Table 4. Holding Times and Temperature/Preservation Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Samples extracted and/or analyzed outside appropriate holding time (< 2× holding time).	J	UJ
2. Samples extracted and/or analyzed outside grossly exceed holding time. (≥ 2× holding time)	J	R
3. Samples received at elevated temperature.	J	UJ
4. Samples collected in unapproved containers.	J	UJ

4.2 SAMPLE-RELATED QUALITY CONTROL RESULTS

4.2.1 Blanks

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. It has been the EPA Region 4 data validation policy to evaluate trip blanks, field blanks, and equipment rinsate blanks as part of the validation process, but not to apply validation codes to the data based on field sample results.

Method Blank

An MB is used to assess the level of contamination that is introduced to the analytical samples throughout the sample preparation and analysis process. **If** contamination is found in any blank, **then** all associated data must be carefully evaluated to determine whether there is a systemic problem affecting greater than one sample or if the contamination is an isolated occurrence.

Instrument Blank

An instrument blank (IB) is used to ensure a stable instrument baseline before analysis of analytical samples.

Field Blank

The project team may elect to collect and analyze a field blank to evaluate the existence and magnitude of contamination that may arise as a result of field-level activities. The field blank provides an indication of ambient conditions during the sampling activities, as well as an indication that the source of decontamination water is free of targeted analytes.

Equipment Rinsate Blank

The equipment rinsate blank provides an indication as to whether nondedicated sampling equipment has been properly decontaminated, and what, if any, carryover may arise between sampled locations.

4.2.1.1 Deliverables

The following are deliverables.

- Blank report summary for all blanks (MB, IB, PB, etc.)
- Raw data (required for confirmation)

4.2.1.2 Frequency

An IB should be analyzed at the beginning of the analytical sequence **and** after the analysis of high-concentration samples and standards (e.g., customer samples, highest calibration standard, calibration verification standard). The MB should be analyzed at a frequency of one per preparatory batch.

4.2.1.3 Criteria

A blank **shall** be considered contaminated **if** detected analytes exceed one-half the reporting limit (RL). The RL is also known as the practical quantitation limit.

4.2.1.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a "B07" validation reason code to the affected data if a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.1.5 Data validation

Verify that results for the blanks are reported accurately on the laboratory summary form from the raw data (Stage 3 and Stage 4 validation only). The data validator **shall** qualify results only if the deviation indicates an adverse effect on data quality.

All laboratory blanks associated with the batch **must** be evaluated against the sample results in the batch; however, qualification should be applied only to those samples directly related to the affected blank (if more than one blank is used per batch).

Any analyte that is reported in both the blank and the sample **must** be evaluated; however, **if** the same analyte is reported in the sample(s) and more than one blank, **then** the sample(s) should be evaluated against the blank with the highest concentration of the analyte.

NOTE: Sample results must **NOT** be modified by subtracting blank values from sample concentrations.

If a blank was **NOT** analyzed with reported samples **or** analyzed of a different matrix than the reported samples, **then** apply an "R" validation code to detected results.

If an analyte was detected in the blank, **then** apply validation codes to data as follows.

- **If** compound is found in a blank **but NOT** an associated sample, **then NO** action is taken.
- **If** an MB was **NOT** analyzed with reported samples, **then** apply an "R" validation code to detected results.
- **If** the sample concentration is greater than the RL **and** blank concentration, **but** the sample concentration is < 5× blank concentration, **then** apply a "J" validation code to detected results.
- **If** both blank concentration **and** sample concentration are greater than the method detection limit (MDL) **and** less than the RL, **then** apply a "U" validation code to detected results.
- **If** the sample concentration is greater than the RL **and** > 5× the blank concentration, **then** no qualification of the data is necessary.
- **If** gross contamination (saturated peaks in blank) is present, **then** apply an "R" validation code to all affected results.

An IB must be analyzed following the analysis of an analytical sample showing saturated signals. **If** this is **NOT** done, **then** the data validator must evaluate the analyses following the saturated sample analysis for carryover. For reported compounds significantly affected by instrument carryover, apply a "J" validation code. **If** gross contamination by instrument carryover is observed, **then** apply an "R" validation code.

For Level IV validation only, conduct raw data confirmation by determining from raw data whether compounds reported in the MB are detected above the RL.

Table 5 summarizes data validation qualification guidance for issues with blanks.

Table 5. Blanks Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. MB **NOT** analyzed.	R	Not applicable (N/A)
2. Sample result > RL **and** ≤ 5× blank result.	J	N/A
3. Sample and blank results > MDL **and** ≤ RL.	U	N/A
4. Sample result > RL **and** ≥ 5× blank result.	N/A	N/A
5. Gross contamination.	R*	N/A
6. IB **NOT** analyzed after sample shows high concentration.	J*	N/A

*Use professional judgment in qualifying data.

4.2.2 Laboratory Control Sample/Laboratory Control Sample Duplicate

An LCS is analyzed to provide accuracy of the analytical method.

4.2.2.1 Deliverable

The following are deliverables for evaluating LCS/LCSDs.

- LCS/LCSD recovery summary
- Raw data (required for confirmation)

4.2.2.2 Frequency

The LCS **shall** be analyzed with each analytical batch to demonstrate proficiency of the method **and must** be repeated when significant changes in instrumentation are made.

4.2.2.3 Criteria

The LCS **must** be analyzed **and must** fall within laboratory-specified limits based on the method used for sample analysis.

EPA Method 1633A

Percent recovery (%R) for the LCS and low-level LCS analyses **must** be within the acceptance limits of Table 5 of EPA Method 1633A for aqueous matrix and Table 7 of EPA Method 1633A for solid, biosolid and tissue matrices (EPA 2024). The LCS **must** contain **all** extracted internal standards, nonextracted internal standards, **and** analytes reported in the sample data.

NOTE: The Method 1633A equivalent to the LCS is the ongoing precision and recovery standard. The Method 1633A equivalent to the low-level LCS is low-level ongoing precision and recovery standard.

EPA Method 537.1

The low-level LCS %Rs **must** be within 50–150% of the true value. The medium and high-level LCS %Rs **must** be within 70–130% of the true value. The LCS **must** contain all nonextracted internal standards **and** analytes reported in the sample data.

4.2.2.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "L05" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.2.5 Data validation

Confirm that the LCS was prepared and analyzed. The following provides guidance for qualification of samples due to poor LCS performance.

- **If** LCS was **NOT** analyzed at the proper frequency, **then** apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.

- **If** LCS was **NOT** prepared **and** analyzed with project samples, **then** apply an "R" validation code to detected and nondetected results.

- **If** the LCS %R for an analyte is greater than acceptance limits, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

- **If** the LCS %R for an analyte is less than acceptance limits, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

- **If** an LCSD is included with the analyses, **and** the calculated relative percent difference (RPD) between the LCS and LCSD results is > 30%, **then** apply a "J" validation code to associated detected results. No qualification is necessary for nondetected results.

- **If** an analyte is **NOT** spiked in the LCS/LCSD, **then** apply an "R" validation code to detected and nondetected results.

Table 6 summarizes data validation qualification guidance for issues with the LCS.

Table 6. LCS Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. LCS **NOT** analyzed at the proper frequency.	J	UJ
2. LCS **NOT** prepared and analyzed.	R	R
3. LCS %R > upper acceptance limit.	J	N/A
4. LCS %R < lower acceptance limit.	J	R
5. LCS and LCSD RPD > 30%.	J	N/A
6. Analyte **NOT** spiked in LCS and/or LCSD.	R	R

4.2.3 Matrix Spike/Matrix Spike Duplicate

The purpose of the MS/MSD is to determine whether the sample matrix contributes bias to the analytical results. **If** the MS/MSD %R criteria are not satisfied, **then** there is difficulty in assessing whether the cause was due to method performance or matrix. To address this issue, LCS and/or LCSD are analyzed to verify method accuracy. **If** only the MS/MSD are affected, **then** a matrix effect is likely.

The data validator may determine that only some of the samples in the data package are similar to the MS sample, and that only these samples should be qualified. The data validator may determine that **NO** samples are sufficiently similar to the sample used for the MS, **and** that only the field sample used to prepare the MS sample should be qualified.

4.2.3.1 Deliverables

The following are deliverables for evaluating MS/MSD.

- MS/MSD recovery summary
- Raw data (required for confirmation)

4.2.3.2 Frequency

MS/MSD are analyzed at a frequency of once per 20 samples of similar matrix and concurrently with the samples in the SDG, unless an MS/MSD analysis is **NOT** required.

4.2.3.3 Criteria

EPA Method 1633A

MS/MSD pairs are **NOT** required for EPA Method 1633A; however, MS/MSD pairs **may** be analyzed **if** requested.

If MS/MSD pairs are requested **and** reported, **then** MS/MSD recovery results **must** be within the acceptance limits of Table 5 of EPA Method 1633A for aqueous matrix and Table 7 of EPA Method 1633A for solid, biosolid and tissue matrices (EPA 2024).

RPDs of the MS/MSD pair analyses **must** be ≤ 30%.

The MS/MSD pair **must** contain all extracted internal standards, nonextracted internal standards, and analytes reported in the sample data.

EPA Method 537.1

Low-level MS/MSD %Rs **must** be 50–150% of the true value. Medium and high-level MS/MSD %Rs **must** be 70–130% of the true value.

RPDs of the low-level MS/MSD pair analyses **must** be ≤ 50%. RPDs of the medium and high-level MS/MSD pair analyses **must** be ≤ 30%.

The MS/MSD pair **must** contain all extracted internal standards, nonextracted internal standards, and analytes reported in the sample data.

4.2.3.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "M05" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.3.5 Data validation

Review the MS/MSD results to determine **if** there is an overall bias to the sample. Data validation of samples and sample groups using the MS/MSD should be conducted in conjunction with other supporting QC data. These generally include initial and continuing calibration checks, LCS, and surrogate standards. The data validator will evaluate MS/MSD performance in conjunction with the other QC data to determine if matrix-specific or instrumental problems are the cause of poor performance. Professional judgment **shall** be used to determine the need for applying validation codes to reported compounds. The data validator **shall** qualify only if the deviation indicates an adverse effect on data quality.

If MS/MSD analysis was required, **but NOT** performed, **then** qualify only **if** the deviation indicates an adverse effect on data quality. Occasionally, limited sample volumes prevent the preparation and analysis of MS/MSDs. In these cases, it is common practice for the laboratory SOW to allow for the analysis of an LCS/LCS duplicate pair as a substitute to provide an evaluation of precision in the measurable range of the method.

In the absence of either the MS/MSD or LCS/LCSD, it is unlikely that a complete evaluation of method precision and accuracy can be completed. In this case, at a minimum, sample results should be considered estimated quantities due to the inability to fully determine the quality of the reported results. Apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results unless other quality deficiencies are observed.

The laboratory **may** also include an MS/MSD analysis performed on a parent sample that is not from the sample set being reviewed in the laboratory data package. This is commonly called a "batch QC sample." The data validator should consult with the SMO to determine whether the batch QC data is applicable to the sample set being validated.

A determination **shall** be made concerning what extent that noncompliant MS/MSD data has on other sample data regarding the sample matrix effect itself, as well as specific compounds in samples associated with the MS/MSD. In those instances where it can be determined that the results of the MS/MSD affect only the parent sample, then qualification **shall** be limited to that sample alone; however, it **may** be determined that the laboratory is having a systematic problem in the analysis of one or more compounds, which affects all associated samples.

If the MS or MSD has been provided **and** recovery difficulties have been noted, **then** the following guidance **shall** be used for evaluating accuracy.

- **If** an analyte is **NOT** spiked in the MS/MSD pair, **then** apply an "R" validation code to detected and nondetected results for analyte **NOT** spiked.

- **If** poor spike recovery occurs in a sample whose concentration is > 4× the spiked amount, **then NO** qualification is necessary.

- **If** the MS %R for an analyte is greater than upper acceptance limit, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

- **If** the MS %R for an analyte is > 10% **and** less than lower acceptance limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the MS %R for an analyte is < 10%, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

If poor MS/MSD precision is observed, **then** the following guidance shall be used.

- **If** the RPD for an MS/MSD pair is > 30%, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

For Level IV validation only, recalculate one MS recovery from raw data for confirmation using equation found in Appendix C.

Table 7 summarizes data validation qualification guidance for issues with the MS/MSD.

Table 7. MS/MSD Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. MS/MSD **NOT** analyzed **and** is required.	J*	UJ*
2. Analyte **NOT** spiked in MS/MSD.	R	R
3. MS %R outside acceptance limits and sample concentration > 4× the spiked amount.	N/A	N/A
4. MS %R > upper acceptance limit.	J	N/A
5. MS %R > 10% and < lower acceptance limit.	J	UJ
6. MS %R < 10%.	J	R
7. MS/MSD RPD > 30%.	J	N/A

*In cases of insufficient sample volume, alternative QC may be used to evaluate precision and accuracy (i.e., LCS/LCSD and laboratory duplicate).

NOTE: For an MS/MSD %R that does not meet the acceptance criteria, apply validation codes to all samples of the same matrix, if the validator considers the samples sufficiently similar. The validator will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, which includes site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity); and laboratory data for other parameters (e.g., total suspended solids, total dissolved solids, total organic carbon, alkalinity or buffering capacity, anions) in determining similarity. The validator should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the laboratory data package. The validator may determine that only some of the samples in the laboratory data package are similar to the MS sample, and that only these samples should be qualified. The validator may determine that no samples are sufficiently similar to the sample used for the MS and, thus, that only the field sample used to prepare the MS/MSD sample should be qualified.

4.2.4 Duplicates

A laboratory duplicate sample is analyzed for each matrix to evaluate the precision of the laboratory at the time of analysis. A field duplicate sample is collected and analyzed to evaluate the precision of both the sampling techniques as well as the laboratory methodology. A field duplicate also may provide information on the homogeneity of the sample. Nonhomogeneous samples can impact the apparent method precision; however, aqueous/water samples are generally homogenous and most soil/sediment samples are homogenous within a factor of two or three.

4.2.4.1 Deliverables

The following are deliverables for evaluating duplicates.

- Laboratory duplicate sample summary
- Raw data (required for confirmation)

4.2.4.2 Frequency

One laboratory duplicate may be analyzed in accordance with the sample methodology used. Typically, a laboratory duplicate is analyzed per each sample batch or once per 20 samples, whichever is more frequent. Field duplicates are collected at a frequency identified in associated project planning documents (e.g., QAPPs).

4.2.4.3 Criteria

The following are criteria for laboratory and field duplicates.

- Samples identified as field blanks or equipment rinsate blanks **must NOT** be analyzed as the laboratory duplicate.

- For sample concentrations ≥ 5× the RL, the RPD precision criteria for aqueous laboratory and field duplicate samples **must** be within ± 30%.

- For sample concentrations ≥ 5× the RL, the RPD precision criteria for solid laboratory and field duplicate samples **must** be within ± 35%.

- **If** the sample results < 5× the RL, **then** RPD does **NOT** apply. Instead, the absolute difference between the sample and duplicate results **must** be less than the RL.

4.2.4.4 Data verification

Verify that field blanks and/or equipment rinsate blanks were **NOT** analyzed as laboratory duplicates. **If** a field blank or equipment rinsate blank has been used as the laboratory duplicate, **then** contact the SMO to have the laboratory address the issue. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem **and shall** be identified as such on the data verification/validation checklist.

Verify the presence of laboratory and field duplicate results. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem **and shall** be identified as such on the data verification/validation checklist.

4.2.4.5 Data validation

The following are data validation steps to evaluate laboratory and/or field duplicates.

- Examine the raw data (if provided) for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility).

- Verify that appropriate methods and amounts were used in preparing the samples for analysis.

- Verify that there are **NO** transcriptions or reduction errors (e.g., dilutions, percent solids, sample weights) on one or more samples.

- Verify that results fall within the linear range(s) of the instrument, if applicable.

The following summarizes data qualification guidance for evaluating laboratory duplicates and field duplicates.

- For aqueous matrix laboratory and field duplicates where sample concentrations are ≥ 5× the RL **and** the RPD between sample and laboratory and/or field duplicate is > 25%, apply a “J” validation code to detected results and apply a “UJ” validation code to nondetected results.

- For solid matrix laboratory and field duplicates where sample concentrations are ≥ 5× the RL **and** the RPD between sample and laboratory and/or field duplicate is > 40%, apply a “J” validation code to detected results and apply a “UJ” validation code to nondetected results.

- For aqueous and solid matrix laboratory and/or field duplicates where sample concentrations are < 5× the RL **and** the calculated absolute difference between sample and duplicate is greater than the RL, apply a “J” validation code to detected results. No qualification is necessary for nondetected results.

Laboratory and field duplicate qualification is provided in Table 8.

Table 8. Laboratory and Field Duplicate Validation Qualification Guidance

Duplicate Type	Matrix	RPD	Sample Results	Validation Qualification Guidance	
				Detects	Nondetects
Laboratory Duplicate	Aqueous	> 25%	Sample and duplicate ≥ 5× RL	J	UJ
	Solid	> 40%			
	Aqueous	N/A (Absolute difference greater than RL)	Sample and duplicate < 5× RL	J	N/A
	Solid				
Field Duplicate	Aqueous	> 25%	Sample and duplicate ≥ 5× RL	J	UJ
	Solid	> 40%			
	Aqueous	N/A (Absolute difference greater than RL)	Sample and duplicate < 5× RL	J	N/A
	Solid				

4.2.5 Surrogate Standards

Surrogate standards are nontarget compounds added to all analytical samples, blanks, and QC samples to assess overall system performance. These standards are added prior to extraction as a means to assess method performance from extraction to final chromatographic measurement. The surrogate standards, perfluoro-n-hexanoic acid, tetrafluoro-2-(heptafluoropropoxy) propanoic acid, perfluoro-n-decanoic acid, and n-ethyl perfluoroctane sulfonamido acetic acid, are used in EPA Method 537.1. Surrogate standards are **NOT** applicable for EPA Method 1633A.

4.2.5.1 Deliverables

The following are deliverable related to surrogate standards.

- Surrogate recovery reports for all samples, blanks, and QC samples
- Raw data (required for confirmation)
- Surrogate list with associated target analytes (if needed)

4.2.5.2 Frequency

Surrogate standards are added to all analytical samples, blanks, and QC samples.

4.2.5.3 Criteria

The surrogate standard %Rs **must** be in the range of 70–130%.

4.2.5.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "S06" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.5.5 Data validation

Evaluate surrogate data to ensure that all reported analytes were spiked and that surrogate %Rs meet acceptance criteria. **If** there are issues with the surrogates, **then** use the following guidance to qualify the data.

- **If** surrogates are **NOT** spiked in sample, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.
- **If** any surrogate %R is greater than the upper control limit, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.
- **If** any surrogate %R is ≥ 10% **and** less than the lower control limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** any surrogate %R is < 10%, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

If surrogates are "diluted out," **then** the data validator **must** use professional judgment to determine whether qualification of data is necessary.

Reanalysis of samples must be inspected to determine which analysis provides the best results. The choice **must** be based on at least the following criteria:

- Surrogate %Rs;
- Holding times;
- Comparison of concentration of target compounds; or
- Internal standard areas and RT.

Table 9 summarizes data validation qualification guidance for issues with surrogate standards.

Table 9. Surrogate Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Surrogate standards **NOT** spiked in sample.	J	R
2. Surrogate %R > upper control limit.	J	N/A
3. Surrogate %R ≥ 10% and < lower control limit.	J	UJ
4. Surrogate %R < 10%.	J	R

4.2.6 Cleanup

Cleanup is performed to remove matrix interferences from sample extracts prior to analysis. Cleanup is applicable to EPA Method 1633A only.

4.2.6.1 Deliverables

The following are deliverables for cleanup.

- Cleanup summary form
- Raw data (required for confirmation)

4.2.6.2 Frequency

Samples of all matrices (and the associated batch QC) **must** undergo solid-phase extraction and carbon cleanup.

4.2.6.3 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "V04" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.6.4 Data validation

Qualify only **if** the deviation indicates an adverse effect on data quality. Use professional judgment when qualifying sample results based on cleanup procedures.

4.2.7 Internal Standards

Internal standards, also known as non-extracted internal standards, are added to samples after extraction and prior to analysis. Isotope dilution standard recoveries are determined by comparison to the responses of one of seven non-extracted internal standards and are used as general indicators of overall analytical quality.

4.2.7.1 Deliverables

The following are deliverables for evaluating internal standards.

- Recovery summary for internal standards
- Raw data (required for confirmation)

4.2.7.2 Frequency

Internal standards are added to all analytical samples, calibration standards, blanks, and QC samples prior to injection of an aliquot of the extract into the LC/MS/MS instrument.

4.2.7.3 Criteria

EPA Method 1633A

The internal standard peak area **must** be within 50–200% of the mean peak area of the corresponding internal standard in the most recent initial calibration.

EPA Method 537.1

The internal standard peak area **must** be within 70–140% of the peak area from the most recent CCV, **NOT** to exceed $\pm$ 50% from the mean peak area measured during initial calibration.

4.2.7.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "I07" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.7.5 Data validation

The following provides guidance for qualification of samples due to poor internal standard performance.

- **If** internal standards are **NOT** added to the sample, **then** apply an "R" validation code to detected and nondetected results.
- **If** internal standards were **NOT** added at correct concentration, **then** use professional and technical judgment in evaluating the data quality effect.
- **If** internal standard peak area is greater than the upper limit, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.
- **If** internal standard peak area is ≥ 30% of the mean peak area from the initial calibration **but** less than the lower limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.
- **If** internal standard peak area is < 30% of the mean peak area from the initial calibration, **then** apply an "R" validation code to detected and nondetected results.
- **If** internal standard RTs vary by more than ± 10 seconds (between the sample internal standard and calibration internal standard), **then** conduct confirmation of raw data for Level IV data validation only by examining the chromatographic profile for that sample to determine if any false positives or negatives exist.
- **If** false positives or negatives exist, **then** use professional judgment to qualify the data.

Table 10 summarizes data validation qualification guidance for issues with internal standards.

Table 10. Internal Standards Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. **No** internal standards added to sample.	R	R
2. Internal standards **NOT** added at correct concentration.	*	*
3. Internal standard peak area > upper limit.	J	N/A
4. Internal standard peak area ≥ 30% **and** < lower limit.	J	UJ
5. Internal standard peak area < 30%.	R	R
6. Internal RTs vary by more than ± 10 seconds.	*	*

*Use professional judgment to qualify.

4.2.8 Isotope Dilution Standards

NOTE: Isotope dilution standards are only applicable for EPA Method 1633A.

The recovery of this spike analysis provides for establishing the performance of the laboratory extraction and analysis. This solution is added to all samples, blanks, and laboratory QC samples prior to extraction. The performance results for isotope dilution standards are critical to the overall accuracy and precision of the analysis because target compound results for each PFAS isomer are quantitated based on the response of the corresponding labeled isomer. Isotope dilution standard recoveries are determined by comparison to the responses of one of seven nonextracted internal standards and are used as general indicators of overall analytical quality. Isotope dilution standards may also be called extracted internal standards.

4.2.8.1 Deliverables

- %Rs for isotope dilution standards
- Raw data (required for confirmation)

4.2.8.2 Frequency

All samples, calibration standards, blanks, and QC samples are fortified with isotope dilution standards. Isotope dilution standards are added prior to extraction.

4.2.8.3 Criteria

The isotope dilution standard %Rs **must** fall within the DoD/DOE QSM limits. **If** DoD/DOE QSM limits are **NOT** available for an isotope dilution standard, **then** use laboratory-developed %R acceptance criteria.

Samples **must NOT** be filtered, **and** subsampling should be avoided **if** possible. The isotope dilution standards **must** be spiked into the original sample container prior to centrifugation.

4.2.8.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Qualify data only **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.8.5 Data validation

Check the raw data to verify reported isotope dilution standard %Rs. Compare the reported %R to the limits in DoD/DOE QSM.

- **If** isotope dilution standards are available **but NOT** used in analysis, **then** apply an "R" validation code to detected and nondetected results of associated target analytes.

- **If** an isotope dilution standard %R is > the upper control limit, **then** apply a "J" validation code to detected results of the associated target analytes. No qualification is necessary for nondetected results.

- **If** an isotope dilution standard %R ≥ 10% **but** less than the lower control limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** an isotope dilution standard %R is < 10%, **then** apply an "R" validation code to detected and nondetected results of associated target analytes.

NOTE: **If** the DoD/DOE QSM lower limit is < 10% for an isotope dilution standard, **then** only apply a "R" validation code to that result **if** the isotope dilution standard %R is less than the DoD/DOE QSM lower limit.

Table 11 summarizes data validation qualification guidance for issues with isotope dilution standards.

Table 11. Isotope Dilution Standards Qualification Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Proper isotope dilution standards NOT used.	R	R
2. Isotope dilution standard %R > upper limit.	J	N/A
3. Isotope dilution standard %R ≥ 10% and < lower limit.	J	UJ
4. Isotope dilution standard %R < 10%. (see note)	R	R

4.3 INSTRUMENT-RELATED QUALITY CONTROL RESULTS

4.3.1 Mass Calibration

4.3.1.1 Deliverables

The following are deliverables for the mass calibration.

- Raw data (required for confirmation)

4.3.1.2 Frequency

The laboratory **shall** calibrate the mass scale of the LC/MS/MS with the calibration compounds and procedures prescribed by the manufacturer.

4.3.1.3 Criteria

The mass calibration verification **must** be performed after each mass calibration. The laboratory **must** follow the instructions for their instrument software to confirm the mass calibration, mass resolution, and peak relative response (RR). **If** the manufacturer's instructions include options for evaluation of mass resolution, **then** the tightest resolution requirements (typically called unit resolution) **must** be met.

4.3.1.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "P05" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.1.5 Data validation

Mass calibration **must** be performed as recommended by the instrument manufacturer to maintain instrument sensitivity and stability. Mass calibration **must** be performed using the calibration compounds and procedures prescribed by the manufacturer. Mass calibration verification should be performed after mass calibration.

If the mass verification fails the manufacturer's instructions, **then** apply an "R" validation code to the detected and nondetected results.

Table 12 summarizes data validation qualification guidance for mass calibration.

Table 12. Mass Calibration Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
Mass verifications **NOT** performed **or** fail manufacturer's instructions.	R	R

4.3.2 Initial Calibration

Compliance requirements for satisfactory instrument calibration ensure that the instrument can produce acceptable qualitative and quantitative data for all target compounds. The objective of the initial calibration is to establish a linear range for the native analytes of interest including their respective isotope dilution standards and nonextracted internal standards. The initial calibration is to be used for routine quantitation of samples using the mean RRs and the mean response factors (RFs) established from the calibration.

4.3.2.1 Deliverables

- Initial calibration summary
- Raw data (required for confirmation)

4.3.2.2 Frequency

Initial calibration **must** be performed before any samples are analyzed for PFAS method analytes.

4.3.2.3 Criteria

The following subsections present the most common requirements for calibration information related to PFAS analysis based on the methods identified in this plan; however, the data validator will need to review the requirements of a specific method and/or the laboratory method that is being reviewed and follow the requirements for that method when validating data. This may mean that the laboratory method will need to be obtained and reviewed prior to data validation. In all cases, specific method requirements for calibration should always be used as the primary guidance when evaluating PFAS data.

EPA Method 1633A

Each calibration standard **must** contain isotope dilution standards and nonextracted internals standards. The lowest concentration standard **must** be at or below the RL. At least six contiguous calibration standards are required for a valid analysis when using a linear calibration model, with at least five of the six calibration standards being greater than or equal to the RL. Additional calibration standards, at levels lower than the lowest calibration standard listed in the method, may be added to accommodate a lower limit of quantitation **if** the instrument sensitivity allows.

One of the following two approaches **must** be used to evaluate the linearity of the instrument calibration:

- Option 1: Calculate the percent relative standard deviation (%RSD) of the RR or RF values for each native compound and isotope dilution standard for all the initial calibration standards that were analyzed. The %RSD **must** be ≤ 20% to establish instrument linearity.

- Option 2: Calculate the percent relative standard error (%RSE) for each native compound and isotope dilution standard for all the initial calibration standards that were analyzed. The %RSE for all method analytes **must** be ≤ 20% to establish instrument linearity.

For all target analytes with exact corresponding isotopically labeled analogs, target analytes **must** elute within ± 0.1 minutes of the associated isotope dilution standard compound. The RTs of each target analyte and isotopically labeled compound **must** be within ± 0.4 minutes of the initial calibration or CCV used to establish the RT windows.

EPA Method 537.1

At least five calibration standards are required for a valid analysis when using a linear calibration model. The lowest concentration standard **must** be at or below the RL, which may depend on system sensitivity. It is recommended that at least four of the standards are at a concentration greater than or equal to the RL.

Calibrate the LC/MS/MS and fit the calibration points with either a linear or quadratic regression.

- Validate the initial calibration by calculating the concentration of each analyte as an unknown against its regression equation. For calibration levels that are less than or equal to the minimum reporting level, the result for each analyte **must** be within ± 50% of the true value. All other calibration points **must** calculate to be within ± 30% of their true value.

Initial calibration **must** be performed at instrument set-up **and** after ICV or CCV failure, prior to sample analysis.

4.3.2.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "C07" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.2.5 Data validation

The data validator shall place the following data validation reason codes to results **if** the following conditions are met. Qualify only **if** the deviation indicates an adverse effect on data quality.

- **If** initial calibration sequence was **NOT** followed, **then** apply "C03" validation reason code.
- **If** appropriate number of standards were **NOT** used, then apply "C24" validation reason code.
- **If** inappropriate concentrations, **then** apply "C18" validation reason code.

Inspect the calibration summary and verify agreement with the raw data (quantitation sheets and chromatograms). Verify the minimum number of calibration standards was used for each analyte. The lowest level calibration standard should be at or below the RL.

For Level IV validation only, check and recalculate at least one of the %RSD values of the mean and standard deviation of the RFs for the labeled and unlabeled standards. Verify that the %RSD for each compound is within the specified range, or that the complete calibration curve was used for quantitation. Alternatively, %RSE for each analyte and its labeled analogue is permissible and should be < 20%.

If an initial calibration has **NOT** been performed, **then** apply an "R" validation code to detected and nondetected results.

EPA Method 1633A

- **If** the %RSE or %RSD for a target analyte is > 20%, **then** apply "J" validation code to detected results and apply a "UJ" validation code to nondetects.

- **If** target analyte is **NOT** within appropriate windows and absolute RT of isotope dilution standard, then use professional judgment to qualify the data. Qualify only if the issue has an adverse effect on data quality.

EPA Method 537.1

- **If** the calibration level is less than or equal to the RL **and** is outside ± 50% of the true value, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the calibration level is greater than the RL **and** is outside ± 30% of the true value, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

For Level IV data validation only, conduct raw data confirmation by inspecting for instances of manual integrations of peak areas. Recurring manual integrations on similar peaks within a calibration, manual integrations on peaks with normally good symmetry, and peak splitting manual integrations **shall** be inspected to determine the necessity for integration or whether a systematic problem is occurring in the analyses.

Confirm the quantitation ions of two compounds in the initial calibration to determine whether the correct quantitation ions have been used to quantify the compounds. **If** incorrect ions have been shown, **then** rationale should be provided in the data package for the noncompliance.

Equations for calculating RF and %RSD are found in Appendix C. **If** calculated RF and %RSD are > 10% error, **then** the data validator should use professional judgment to determine impact on data **and** provide an explanation for the qualification made to the data.

Raw data **must** be consulted before qualifying data based on initial calibration alone. Checks **must** be made for saturation, baseline shift, peak splitting, ion ratios, and other obvious interferences. **If** anomalies are found in the raw data, **then** use professional judgment in qualifying data.

Table 13 summarizes data validation qualification guidance for the initial calibration.

Table 13. Initial Calibration Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Initial calibration **NOT** performed.	R	R
2. %RSE or %RSD for target analyte > 20%. (EPA 1633A)	J	UJ
3. Calibration level ≤ RL and outside ± 50% of true value (EPA 537.1)	J	UJ
4. Calibration level > RL and outside ± 30% of true value (EPA 537.1)	J	UJ
5. Target analyte **NOT** within appropriate windows **and** absolute RT of isotope dilution standard. (EPA 1633A only)	*	*
6. Anomalies found in raw data (Level IV validation only).	*	*
7. Quantitation ions of 2 compounds are NOT at the correct ions for quantitation (Level IV validation only)	*	*

*Use professional judgment to qualify data.

4.3.3 Initial and Continuing Calibration Verification

ICVs and CCVs ensure that the instrument is capable of consistently producing acceptable qualitative and quantitative data. The instrument is checked over specific time periods during the sample analysis.

4.3.2.1 Deliverables

- Continuing calibration (ICV/CCV) summary
- Raw data (required for confirmation)

4.3.2.2 Frequency

Calibration is verified for PFAS initially following calibration using a mid-level calibration standard and an instrument sensitivity check (ISC) (lowest level calibration standard equal to or less than RL). An ISC **must** be analyzed prior to sample analysis. The continuing calibration standard **must** be analyzed prior to sample analysis **and** after every 10 field samples or less throughout an analytical sequence, **and** at the end of the analytical sequence. An ISC **must** be analyzed at the beginning of each analytical sequence **and** every 12 hours.

4.3.2.3 Criteria

EPA Method 537.1

The mid and high-level CCV, percent difference (%D) or percent drift for each target analyte and surrogate should be within ± 30% **and** the %D of the lowest calibration point for each target analyte and surrogate should be within ± 50%.

EPA Method 1633A

The ICV, ISC, and CCV %D or percent drift for each target analyte and isotope dilution standard should be within ± 30%.

The CCV does **NOT** have to be second sourced **and** should be a mid-level calibration standard or low-level calibration standard. **If** the initial daily CCV is analyzed at the RL, **then** it can also serve as the first ISC of the analytical sequence.

4.3.2.4 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue **CANNOT** be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an "C07" validation reason code to the affected data **if** a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.2.5 Data validation

If the ICV/CCV or ISC were **NOT** analyzed at the correct frequency, **then** use professional judgment to qualify data. Qualify data only if the issue has an adverse effect on data quality.

If the %D exceeds ICV/CCV criteria, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

For Level IV validation only, conduct raw data confirmation by confirming the quantitation ions of two compounds in the CCV to determine whether the correct quantitation ions have been used to quantify the compounds. **If** incorrect ions have been shown, **then** rationale should be provided in the laboratory data package for the noncompliance.

Table 14 summarizes data validation qualification guidance for issues with the ICV/CCV and ISC.

Table 14. ICV/CCV Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. ICV/CCV and/or ISC **NOT** analyzed at correct frequency.	*	*
2. ICV/CCV %D exceeds criteria.	J	UJ

*Use professional judgment to qualify data.

4.4 RECALCULATION CHECKS

The accuracy and consistency of sample result calculation by the laboratory can be addressed using two different techniques. The application of each strategy depends on the laboratory's ability to minimize transcription during reporting and how familiar the project is with the performance of the laboratory.

If the laboratory has a high rate of manual transcription in generation of sample results, **then** the project **may** choose to manually recalculate sample results at a determined frequency. **If** sample results cannot be reproduced through manual calculation, **then** contacting the laboratory may be necessary to resolve the problem. "R" validation codes may be applied to data as a last resort, **if NO** actions can reproduce reported values. For Stage 3 and Stage 4 validation only, **if** recalculations are performed, **then** recalculate one sample result from raw data for confirmation.

4.4.1 Reporting Limits/Sample Quantitation Limits

RLs have been developed to enable the laboratory to meet realistic detection limit goals. RLs should be greater than or equal to the lowest calibration standard used in the initial calibration.

Due to deviations from method-specified sample weights, extract volume or aliquot used in analysis or due to dilution or soil % moisture, RLs are modified accordingly and are termed sample quantitation limits (SQLs).

4.4.1.1 Deliverables

The following is a deliverable for evaluation of RLs and SQLs.

- Sample summary/sample data sheets

4.4.1.2 Frequency

RLs or SQLs are reported for all compounds.

4.4.1.3 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the laboratory and request that they be provided. **If** these occurrences **CANNOT** be resolved with the analytical laboratory, **then** they are considered uncorrectable problems.

4.4.1.4 Data validation

For one nondetect compound in each sample blank, verify that the RLs have been adjusted for deviation from the nominal preparation and analysis conditions, such as sample size and aliquot, if necessary.

4.4.2 TARGET COMPOUND IDENTIFICATION AND QUANTITATION

A target analyte or isotope dilution standard is identified in a standard, blank, sample, or QC sample when all of the criteria below are met.

4.4.2.1 Deliverables

- Sample summary/sample data sheets
- Raw data (required for confirmation)

4.4.2.2 Criteria

For target analytes or surrogates/isotope dilution standards to be identified, peak responses of the quantitation and confirmation ions must be at least three times the background noise level [signal-to-noise ratio (S/N) 3:1]. The quantitation ion must have an S/N ≥ 10:1 **if** there is **NO** confirmation ion. The quantitation ion used **must** be the quantitation ion identified in the method, unless interferences are presently affecting the quantitation ion.

Target analyte, isotope dilution standards, and internal standards RTs **must** fall within ± 0.4 minutes of the predicted RTs from the mid-point standard of the initial calibration or ICV, whichever was used to establish the RT window position for the analytical batch.

For all target analytes with exact corresponding isotopically labeled analogs, target analytes must elute within ± 0.1 minutes of the associated isotopically labeled analogs.

For concentrations at or above the method RL, the ion area ratio (IAR) **must** fall within ± 50% of the IAR observed in the mid-point initial calibration standard.

Examine the raw data (if provided) for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility). Verify that results fall within the linear range(s) of the instrument, if applicable.

The laboratory **must** demonstrate a separation of at least 1 minute between the bile salt interference check standard containing taurodeoxycholic acid and the RT window of any of the linear or branched perfluorooctanesulfonic acid isomers. The frequency of the bile salt interference check should be performed after an initial calibration and with each analytical batch.

4.4.2.3 Data verification

Verify the presence of required reporting forms. **If** they are **NOT** provided, **then** contact the SMO and request that they be provided. **If** these occurrences **CANNOT** be resolved with the analytical laboratory, **then** they are considered uncorrectable problems, indicate this on the data verification checklist.

4.4.2.4 Data validation

Verify that appropriate methods and amounts were used in preparing the samples for analysis.

Verify that there are **NO** transcriptions or reduction errors (e.g., dilutions, percent solids, sample weights) on one or more samples.

The presence/absence and concentration of detected compounds in the samples are reviewed to determine whether the correct quantitation ions have been used for proper quantification of the compounds and proper peak integration.

If incorrect ions have been shown, **then** the rationale should be provided in the laboratory data package for the noncompliance. **If NO** rationale has been provided, **then** apply an "R" validation code to detected and nondetected results.

If the sample was analyzed from a diluted extract, **then** the isotope dilution standard %Rs from the analysis of the diluted extract **must** be > 5% to quantify the associated target compounds. Concentration, MDLs, and RLs must be adjusted to account for the dilution.

If the sample results do **NOT** meet the criteria above excluding quantitation ion criteria, **and** all sample preparation avenues (e.g., extract cleanup, sample dilution) have been exhausted, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results. This will alert the data user that the result could **NOT** be confirmed because it did **NOT** meet the method-required criteria and, therefore, should be considered an estimated value.

Inspect the data for instances of manual integrations of peak areas. Reoccurring manual integrations on similar peaks from sample to sample or from calibration to sample, or on peaks with normally good peak resolution, or for splitting of peaks should be inspected to determine the necessity for integration, or whether a systematic problem is occurring in the analyses.

Situations that may tend to produce carryover to subsequent sample analyses, such as the analysis of samples showing high concentrations of compounds, shall be evaluated. **If** cross-contamination has an effect on a compound, such as reporting of false positives or artificially elevating compound levels, **then** an "R" validation code may be applied to the affected data. Qualify data only if there is an adverse effect on data quality.

Samples are diluted and reanalyzed **if** compound signals exceed the dynamic range of the instrument (saturation) or **if** interferences preclude accurate quantitation of compounds. **When** a sample is reanalyzed and both analyses of that sample are included in the laboratory data package, **then** indicate in the data validation report which results are the most reliable.

Table 15 summarizes data validation qualification guidance for issues with the ICV/CCV.

Table 15. Target Compound Identification Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Incorrect quantitation ion used for target analyte	R	R
2. Target compound identification criteria not met.	UJ	J
3. Sample affected by possible carryover.	R*	N/A

*Use professional judgment in qualifying data.

5. RECORDS

Generate and maintain all records in accordance with CP3-RD-0010, *Records Management Process*, which include the following.

- Data verification/validation checklist (Stage 2B, Stage 3, and Stage 4 validation)
- Data validation report (Stage 2B, Stage 3, and Stage 4 validation)

6. REFERENCES

NOTE: Use the most current version of the references that are listed below for data review, verification, and validation processes.

DoD/DOE (U.S. Department of Defense and U.S. Department of Energy) 2023. *Department of Defense and Department of Energy Quality Systems Manual for Environmental Laboratories Version 6.0*, U.S. Department of Defense Environmental Data Quality Workgroup and U.S. Department of Energy Consolidated Audit Program, Washington, DC, December.

EPA (U.S. Environmental Protection Agency) 2020. *Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)*, EPA Method 537.1, U.S. Environmental Protection Agency Washington, DC, March.

EPA 2021. *Method 8327: Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)*, SW-846 Update VII, U.S. Environmental Protection Agency, Washington, DC, July.

EPA 2024. *Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS*; EPA Method 1633A; U.S. Environmental Protection Agency, Washington, DC, December.

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APPENDIX A

DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

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A.1. DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

Data Validation Codes

U The analyte was analyzed for, but was not detected above the reported sample quantitation limit (SQL).

J The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

NJ Presumptively present at an estimated quantity [use with tentatively identified compounds (TICs) only].

UJ Analyte, compound, or nuclide not detected above the reported detection limit, and the reported detection limit is approximated due to quality deficiency.

R Result rejected by validator.

= Validated result, no additional qualifier necessary.

X Not validated; Refer to the RSLTQUAL field for more information.

Data Validation Reason Codes

Blanks

B01 Sample concentration was less than the reporting limit (RL), and ≤ 5× the blank concentration (10× for common contaminants).
B02 Sample concentration was greater than the RL, and ≤ 5× the blank concentration (10× for common contaminants).
B03 Gross contamination exists; blank result impacted associated analyte data quality.
B04 Negative blank result impacted associated analyte data quality.
B05 Blanks were not analyzed at appropriate frequency.
B06 Sample not significantly different than radiochemical method blank.
B07 Blank data not reported.
B08 Instrument blank not analyzed after high-level sample.
B09 Other (describe in comments)
B10 Method blanks not extracted at appropriate frequency.
B11 Sample results were corrected for blank contamination.
B12 Blank was not the same matrix as the analytical samples.
B13 Concentration of target compound detected in sample affected by carryover.

Calibration

C01 Initial calibration average relative response factor (RRF) was < 0.05 or < 0.01 for poor response compounds
C02 Initial calibration percent relative standard deviation was exceeded
C03 Initial calibration sequence was not followed as appropriate
C04 Continuing calibration RRF was < 0.05 or < 0.01 for poor response compounds
C05 Continuing calibration percent difference (%D) was exceeded
C06 Calibration or performance check was not performed at the appropriate frequency
C07 Calibration data not reported

Calibration (continued)

C08 Calibration not performed
C09 Chemical resolution criteria were not satisfied
C10 Calibration standard matrix not the same as sample matrix
C11 Compounds quantitated against inappropriate standard or standard concentration level
C12 Compound quantitated against inappropriate ion
C13 Calibration factor relative standard deviation criteria were not satisfied
C14 Retention time of compound outside window
C15 Initial calibration percent recovery (%R) was below lower acceptance limit
C16 Initial calibration %R was above upper acceptance limit
C17 Initial calibration curve fit was < 0.995
C18 Inappropriate standard concentrations
C19 Continuing calibration %R was below the lower acceptance limit
C20 Continuing calibration %R was above the upper acceptance limit
C21 Contract-required detection limit %R was below the lower acceptance limit
C22 Contract-required detection limit %R was above the upper acceptance limit
C24 Standard curve was established with fewer than the appropriate number of standards
C27 Calibration verification efficiency outside control criteria
C28 Calibration verification background outside control criteria
C29 Calibration verification energy outside control criteria
C30 Calibration verification peak resolution outside control criteria
C31 Chromatogram does not show adequate gain setting
C32 Other (describe in comments)

Laboratory Duplicate/Dual Column Sample Confirmation

D01 Significant difference between sample and duplicate
D02 Laboratory duplicate was not analyzed at the appropriate frequency
D03 Laboratory duplicate exceeds relative percent difference (RPD) criteria
D04 Laboratory duplicate data not reported
D05 Other (describe in comments)
D06 %D between primary and secondary column confirmation exceeds acceptance criteria

Evidentiary Concerns

E01 Custody of sample in question
E02 Standard not traceable
E03 Other (describe in comments)

Interference Check Samples (ICS)

F01 ICS recovery below lower control limit or advisory limit
F02 ICS recovery above upper control limit or advisory limit

General

G01 Professional judgment was used to qualify the data
G02 Other (describe in comments)

Holding Times/Preservation

H01 Extraction holding times were exceeded
H02 Extraction holding times were grossly exceeded
H03 Analysis holding times were exceeded
H04 Analysis holding times were grossly exceeded
H05 Samples were not preserved properly

Holding Times/Preservation (continued)
H06 Sample preservation cannot be confirmed
H07 Sample temperature exceeded criteria prior to preparation
H08 Other (describe in comments)

Internal Standards
I01 Area count was above upper control limits
I02 Area count was below lower control limits
I03 Extremely low area counts or performance was exhibited by a major drop-off
I04 Internal standard retention time varied by more than 30 seconds
I05 Inappropriate internal standard used
I06 Inappropriate internal standard concentration(s) used
I07 Internal standard data not reported
I08 Other (describe in comments)

Laboratory Control Sample (LCS)
L01 LCS recovery above upper control limit
L02 LCS recovery below lower control limit
L03 LCS was not analyzed at appropriate frequency
L04 LCS not the same matrix as the analytical samples
L05 LCS data not reported
L06 Other (describe in comments)

Matrix Spike (MS) and Matrix Spike Duplicate (MSD)
M01 MS and/or MSD recovery above upper control limit
M02 MS and/or MSD recovery below lower control limit
M03 MS/MSD pair exceeds the RPD limit
M04 MS and/or MS/MSD not analyzed at the appropriate frequency
M05 MS and/or MS/MSD data not reported
M06 Other (describe in comments)

Instrument Performance
P01 High background levels or a shift in the energy calibration were observed
P02 Extraneous peaks were observed
P03 Loss of resolution was observed
P04 Peak tailing or peak splitting that may result in inaccurate quantitation were observed
P05 Instrument performance data not reported
P06 Instrument performance not analyzed at the appropriate frequency
P07 Other (describe in comments)
P08 Resolution check mixture (RCM) not analyzed at the beginning of the initial calibration sequence
P09 RCM criteria were not met
P10 RPD criteria in performance evaluation mixture was not met

Quantitation
Q01 Peak misidentified
Q02 Target analyte affected by interfering peak
Q03 Qualitative criteria were not satisfied
Q04 Cross contamination occurred
Q07 Analysis occurred outside 12-hour gas chromatography/mass spectrometry window
Q09 Tentatively identified compound (TIC) result was not above 10 × the level found in the blank
Q10 TIC reported as detect in another fraction

Quantitation (continued)

Q11 Common artifact reported as a TIC
Q12 No raw data were provided to confirm quantitation
Q13 Minimum detectable activity (MDA) greater than RL
Q14 Inappropriate aliquot sizes were used
Q15 Sample result less than MDA
Q16 Sample result less than 2σ uncertainty
Q17 Negative result
Q18 Compounds were not adequately resolved
Q19 Sample geometry different from calibration geometry
Q20 Sample weight greater than greatest weight on mass attenuation curve
Q21 Isotopes of same radionuclide do not show equilibrium
Q22 Peak not within appropriate energy range
Q23 Counting uncertainty ≥ 80% of sample result
Q24 Raw data anomaly
Q25 Other (describe in comments)
Q26 Retention Time (RT) outside calculated RT window
Q28 Neither RL or the sample quantitation limit (SQL) are reported for a nondetect result
Q29 SQL greater than RL
Q30 Compound detected at less than SQL and not qualified "J"
Q31 Presence of high molecular weight contaminants impacted sample quantitation

Surrogates

S01 Surrogate recovery was above the upper control limit
S02 Surrogate recovery was below the lower control limit
S03 Surrogate recovery was < 10%
S04 Inappropriate surrogate standard used
S05 Inappropriate surrogate standard concentration(s) used
S06 Surrogate data not reported
S07 Surrogate outside retention window
S08 Other (describe in comments)

Instrument Tuning

T01 Mass calibration ion misassignment
T02 Mass calibration was not performed every 12 hours
T03 Mass calibration did not meet ion abundance criteria
T04 Mass calibration data was not reported
T05 Scans were not properly averaged
T06 Other (describe in comments)

Pesticide Sample Cleanup

U01 Florisil performance requirements not met
U02 Gel permeation chromatography (GPC) calibration not checked at required frequency
U03 GPC calibration criteria not met
U04 GPC blank not analyzed after GPC calibration
U05 GPC blank greater than half the RL for target compound

Cleanup

V01 10% recovery or less was obtained during either check
V02 Recoveries during either check were > 120%
V04 Cleanup data not reported

Cleanup (continued)

V05 Cleanup check not performed at the appropriated frequency
V06 Other (describe in comments)

Dilutions

X01 Serial dilution not analyzed at the appropriate frequency
X02 %D between the original sample and the diluted result (or serial dilution) exceeded acceptance criteria
X03 Reported results not corrected for dilution factor
X04 Other (describe in comments)

Radiochemical Yield

Y01 Radiochemical tracer yield was above the upper control limit
Y02 Radiochemical tracer yield was below the lower control limit
Y03 Radiochemical tracer yield was zero
Y04 Radiochemical yield data was not present
Y05 Other (describe in comments)

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APPENDIX B

QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

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B.1. QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

This appendix provides guidance in the qualification of data due to instances of multiple quality deficiencies. Quality deficiencies can be categorized based on potential effect on sample data. The effect of quality deficiencies may be applicable to only a single sample or to all samples within the reporting batch. A validation qualifier should **NOT** be placed on sample data until all quality deficiencies have been identified within the reporting batch.

The following is a listing of data quality indicators and the probable effects on sample data.

Data Quality Indicator	Effect on Sample Data
Instrument performance check	Identification and quantitation
Initial calibration	Quantitation
ICV/CCV	Quantitation
MB	Positive bias
Isotope dilution standard	Positive or negative bias
LCS	Method bias
MS/MSD	Positive or negative bias and precision
Internal standard	Positive or negative bias
Cleanup	Quantitation

In the instance of multiple quality deficiencies, the validation qualifier should be placed consistent with the acceptable level of uncertainty associated with the intended use of the data. The validation statement of work should provide a summary of the intended use(s) of the data. (e.g., risk assessment, fate and transport modeling, waste management) to facilitate appropriate placement of validation qualifiers.

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APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

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C.1. RULES, CALCULATIONS, AND EQUATIONS

Rounding Rules

1. In a series of calculations, carry the extra digits through to the final result, and then round off.
2. **If** the digit to be removed is < 5, **then** the preceding digit stays the same.
3. **If** the digit to be removed is = or > than 5, **then** the preceding digit is increased by 1.

Calculations/Equations

C.1 Isotope Dilution Standard and Surrogate Recovery

$$\%R = \left(\frac{A}{B}\right) \times 100$$

where:
A = calculated isotope dilution standard or surrogate concentration for the sample
B = fortified concentration of the isotope dilution standard or surrogate

C.2 Percent Recovery

$$\%R = \left(\frac{A-B}{C}\right) \times 100$$

where:
A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration.

C.3 For Duplicate Measurements

$$\%R = \left(\frac{|FD1-FD2|}{(FD1+FD2)/2}\right) \times 100$$

where:
FD1 = Result 1
FD2 = Result 2

C.4 Mean Relative Response (RR) or Response Factor (RF)

$$\text{mean RR or RF} = \frac{\sum_{i=1} n(RR\ or\ RF)_i}{n}$$

where:
RR_i = Relative Response for calibration standard *i*
RF_i = Response Factor for calibration standard *i*
n = Number of calibration standards

C.5 Standard Deviation

$$\text{SD} = \sqrt{\frac{\sum_{i=1} n((RR\ or\ RRF_i - mean\ RR\ or\ RRF)^2)}{n}}$$

C.6 Relative Standard Deviation

$$\%\text{RSD} = \frac{SD}{mean} \times 100$$

C.7 Relative Standard Error

$$\%\text{RSE} = 100 \times \sqrt{\sum_{i=1}^{n} \frac{[\frac{x' - x_i}{x_i}]^2}{n-p}}$$

where:
x_i = Nominal concentration (true value) of each calibration standard
x' = Measured concentration of each calibration standard
n = Number of standard levels in the curve
p = Type of curve (2 = linear, 3 = quadratic)

C.8 Concentration of Native Analyte

$$\text{Concentration (ng/L or ng/g)} = \frac{Area_n M_{EIS}}{Area_{EIS(RR\ or\ RF)}} \times \frac{1}{W_S}$$

where:

$Area_n$ = The measured area of the Q1 m/z for the native (unlabeled) PFAS
$Area_{EIS}$ = The measured area at the Q1 m/z for the isotope dilution standard
M_{EIS} = The mass of the EIS added (ng)
RR = Average response ratio used to quantify target compounds by the isotope dilution standard
RF = Average response factor used to quantify target compounds by the isotope dilution standard
Ws = Sample volume (L) or weight (g)

C.9 Concentration of Extracted Internal Standard Analyte

$$\text{Concentration (ng/L or ng/g)} = \frac{Area_{EIS} M_{NIS}}{Area_{NIS(RF_S)}} \times \frac{1}{W_S}$$

where:

$Area_{EIS}$ = The measured area at the Q1 m/z for the isotope dilution standard
$Area_{NIS}$ = The measured area of the Q1 m/z for nonextracted internal standard
M_{NIS} = The mass of the nonextracted internal standard added (ng)
RF_S = Average response factor used to quantify the isotope dilution standard by the nonextracted internal standard method
Ws = Sample volume (L) or weight (g)

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