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CP2-ES-2000/FR0

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

DOE CONTRACTOR PERSONNEL ONLY

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

Date Issued—August 2023

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

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Approved by:

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TABLES

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ACRONYMS

%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
CCV	continuing calibration verification
CLP	contract laboratory program
COC	chain of custody
DQO	data quality objective
EDD	electronic data deliverable
EIS	Extracted Internal Standard
EPA	U.S. Environmental Protection Agency
ERI	equipment rinsate blank
FB	field blank
HDPE	high density polyethylene
IAR	ion area ratio
IB	instrument blank
IC	initial calibration
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
NIS	non-extracted internal standard
PFAS	per- and polyfluoroalkyl substances
QAPP	quality assurance project plan
QC	quality control
RDL	required detection limit
RL	reporting limit
RPD	relative percent difference
RR	relative response
RRF	relative response factor
RSD	relative standard deviation
RSE	relative standard error
RT	retention time
S/N	signal-to-noise ratio
SDG	sample delivery group
SMO	sample management office
SOW	statement of work
SPE	solid-phase extraction
SQL	sample quantitation limit

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DEFINITIONS

NOTE 1: Qualifier 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" is 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.

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

Analytical Data Verification—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.

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 have been collected over a given time period from a particular site. A case consists of one or more sample delivery groups.

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

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

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

Correctable Problem—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 revealed during verification are those deficiencies that can be addressed by obtaining additional information from the laboratory. Correctable problems 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 (DQO)—Qualitative and quantitative statements derived from the outputs of each step of the DQO process that specify the study objectives, domain, limitations, the most appropriate type of data to collect, and specify the levels of decision error that will be acceptable for the decision.

Data Quality Objectives (DQOs) Process—A quality management tool based on scientific method and developed by the U.S. Environmental Protection Agency to facilitate the planning of environmental data collection activities. The DQO 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.

Extracted Internal Standard (EIS)—An isotopically labeled analog of a target analyte that is structurally identical to a native (unlabeled) analyte. The EISs are added to the sample at the beginning of the sample preparation process and are used to quantify the native target analytes.

Holding Time—The period of time between sample collection and sample activity determination.

Initial Calibration (IC)—The standardization of a liquid chromatography/tandem mass spectrometry (LC/MS/MS) instrument against a traceable standard of known identity and quantity. This standardization prevails until such time as 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 PFAS standard, blank, matrix strike (MS), 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 compound.

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 PFAS 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.

Laboratory Control Sample (LCS)—A control sample of known composition. Aqueous and solid LCSs are analyzed using the same preparation, reagents, and method employed for field samples.

Laboratory Duplicate—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 Strike (MS)—A split of a field-originating analytical samples in which one half of the split is spiked with a known amount of analyte of interest prior to sample preparation. The purpose of a MS is to measure the effect of interferences from the sample matrix that will preclude accurate quantitation by the instrumentation.

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

Minimum Reporting Limit—The smallest measured concentration of a substance that can be reliably measured by using a given analytical method.

Non-Extracted Internal Standard (NIS)—Labeled PFAS compounds spiked into the concentrated extract immediately prior to injection of an aliquot of the extract into the LC/MS/MS.

Per- and Polyfluoroalkyl Substances (PFAS)—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.

Preparation Batch—A group of sample aliquots prepared together using the same method and related to the same quality control samples.

Quality Indicator Sample—Samples made ready in the laboratory and provide direct or indirect evaluation of the status of the analytical system and resulting data quality. Collectively, quality indicator samples are the LCS, laboratory duplicate, MS, and MB.

Relative Percent Difference (RPD)—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 (RSD)—Measure of precision between multiple values, defined as the standard deviation of multiple values divided by the mean of the values.

Required Detection Limit (RDL)—A contractually specified detection limit that, under typical analytical circumstances, should be achievable.

Reporting Limit (RL)—A contractually specified detection limit that, under typical analytical circumstances, should be achievable.

Sample Delivery Group (SDG)—Defined by one of the following, based on 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 SDG.

Sample Quantitation Limit (SQL)—Detection limits based on the RDL that 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 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 (S/N)—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.

Statement of Work (SOW)—The validation SOW is a document prepared to function as the mechanism by which validation requirements are communicated from the project to the validation organization.

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

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

Uncorrectable Problem—Deficiencies within data packages that preclude the evaluation of data quality by predefined criteria. Uncorrectable problems may be revealed during both data verification and data validation.

Validation Qualifier—A qualifier 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—A document prepared to function as the mechanism by which validation implementation requirements are communicated from the project to the validation organization.

1. INTRODUCTION

1.1 PURPOSE, SCOPE, AND APPLICATION

1.1.1 Purpose

This plan defines the minimum requirements, responsibilities, and methodology for the per- and polyfluoroalkyl substances (PFAS) analysis data verification and validation processes for evaluating analytical data generated using liquid chromatography/tandem mass spectrometry (LC/MS/MS).

This plan provides requirements for developing and implementing a validation methodology for PFAS [U.S. Environmental Protection Agency (EPA) Method 537.1 and Draft Method 1633] analytical methods primarily for analytes in aqueous and soil/sediment matrices (EPA 2020a, EPA 2022). It is flexible enough to allow evaluation of data usability for project-specific data quality objectives (DQOs). 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 contained herein, data validators are advised to seek guidance in the specific method employed and/or from other industry standards. Examples include EPA, Contract Laboratory Program (CLP), National Functional Guidelines for Organic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

Specifications in this plan should be incorporated into project documentation such as the quality assurance project plan (QAPP), into contractual statements of work (SOWs) between the project and the analytical laboratories, and into contractual validation SOWs between the project and the organization chosen to validate the data. **If** data validation is performed by individuals within the project, **then** the SOW is **NOT** required, but a mechanism to specify validation requirements is recommended. This plan shall be used as a baseline to create project-specific reports needed to perform PFAS data verification and validation.

1.1.2 Scope and Application

This plan applies to PFAS data verification and validation activities performed by the sample management office (SMO) or its subcontractors.

2. RESOURCES

- Analytical method
- Laboratory SOW
- Data validation SOW
- Project-specific QAPP

3. PREPERFORMANCE ACTIVITIES

Project manager shall ensure that individuals who perform PFAS data verification and validation are knowledgeable of the latest version of this plan before beginning any activities.

4. GENERAL INFORMATION

4.1 REQUIRED ELEMENTS OF REVIEW AND VALIDATION

To the extent possible, all laboratory data packages will be produced by the laboratory performing the analysis as Level IV (i.e., EPA Stage 4) laboratory data deliverables. All (100%) of the data deliverables will undergo a data quality review and validation comparable to a Level I validation (depending on analyte and method). As required by project-specific requirements, the data review and validation effort may be increased to cover a Level II, Level III, or a full Level IV validation of the data package. The activities included in the review and validation effort for each level are provided in Table 1.

Table 1. Required Elements of Review and Validation

Report Elements to be Reviewed*	**Level I**	**Level II**	**Level III**	**Level IV**
Cover/Signature Page	x	x	x	x
Table of Contents			x	x
Report Narrative	x	x	x	x
Executive Summary (**if** included)			x	x
Method Summary/Analyst Summary			x	x
Sample Summary/Sample Data Sheets	x	x	x	x
Shipping and Receiving Documents	x	x	x	x
Client Chain of Custody (COC)	x	x	x	x
Sample Receipt Checklist	x	x	x	x
Interlab COC (where applicable)		x	x	x
Internal COC (**if** required)			x	x
Glossary of Abbreviations	x	x	x	x
Quality Control (QC) Results				
QC Association Summary		x	x	x
Laboratory Chronicle			x	x
Surrogate and/or Tracer and Carrier Recovery Report		x	x	x
Blank Reports		x	x	x
Laboratory Control Sample (LCS) Reports		x	x	x
MS/MSD and Duplicate Reports		x	x	x
Hold Times and Preservation Requirements	x	x	x	x
Extended Data Deliverables/Forms				
CLP-Like Organics				
SUMMARY FORMS			x	x
Summary Forms (Org I–X)			x	x
QC SUMMARY			x	x
QC Forms (Org I–IV, VIII)			x	x
SAMPLE DATA			x	x

Table 1. Required Elements of Review and Validation (Continued)

Report Elements to be Reviewed*	Level I	Level II	Level III	Level IV
Quantity Report + Chro + Spectra				x
STANDARDS DATA			x	x
Calibration Forms (VI–VII; for GC, VIII–X)			x	x
(Quantity + Chro follows each formset)				x
QC DATA			x	x
Tune			x	x
Blank Form I			x	x
Blank Quantity Report + Chro + Spectra				x
LCS/Laboratory Control Sample Duplicate (LCSD) Form I			x	x
LCS/LCSD Quantity Report + Chro + Spectra				x
MS/MSD Form I			x	x
MS/MSD Quantity Report + Chro +Spectra				x
GEL Permeation Data				x
Florisil Data				x
Logs—Instrument, Prep, Standard			x	x
CLP-Like Inorganics				
Cover Page			x	x
Sample Forms (I) (CLP-like)			x	x
Calibration + QC Forms (exp.: II–XIV)			x	x
Instrument Data				x
Preparation Data				x
SHIPPING/RECEIVING DOCUMENTS				
Internal COC (**if** required)			x	x
Interlab COC (where applicable)			x	x
Client COC	x	x	x	x
Sample Receipt Checklist	x	x	x	x

*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 data package.

The requirements of Level I and Level II review and validation effort will be referred to "data verification" and will be performed by a member of the SMO. The requirements of the Level III and Level IV review and validation effort will be referred to as "data validation," and typically is performed by an entity external to the project. This can be an internal staff member who is **NOT** associated with the project, or it may be an independent third-party external to the Paducah Site. The following sections summarize the requirements of each type of review and validation efforts.

4.2 DATA VERIFICATION REQUIREMENTS

Data verification is defined as a systematic process, performed either by the data generator (on-site or fixed-base laboratory) or by an entity external to the data generator, which results in the evaluation of the completeness, correctness, consistency, and compliance of a data set against a standard or contract.

If data verification is performed by the data generator, **then** a project-level surveillance must be established by which the performance of the verification process is evaluated.

Data verification, at the project level, is conducted by an SMO representative to expedite the review process. **If** data verification is conducted independently of the data validator, **then** it includes two activities. The first activity entails inventory of the data package to ensure compliance with the Contract and SOW, in terms of the required deliverables. The second activity entails various checks of the data quality to determine the need for qualification. This process is commonly referred to as the "contractual screen" and is the beginning of the data validation process in that it encompasses the review of the Level I and Level II validation elements identified in Table 1 above. The data verifier will qualify data based on the review and validation elements in accordance with Section 5 of this plan. **If** the data set is being reviewed and validated at the Level III or IV requirements, **then** the data verifier will provide a copy of the data verification checklist to the data validator to expedite the validation process, or the data validator will perform both the data verification and the data validation processes.

Data verification should provide a mechanism for problem resolution with the laboratory; it should NOT be exclusively an after-the-fact identification of uncorrectable deficiencies.

A data verification checklist is completed by the data verifier and takes, as input, the steps in this plan that are listed as "data verification." The data verifier shall complete Form CP3-ES-5003-F03, *Data Verification Checklist*," in accordance with CP3-ES-5003, *Quality Assured Data,* for all Level II, III, and IV validations.

4.3 ANALYTICAL DATA VALIDATION REQUIREMENTS

Analytical data validation, including laboratory data review, is defined as a systematic process, performed externally from the data generator, which applies a defined set of performance-based criteria to a body of data to determine the quality of reported results. Data validation is **NOT** performed by the analytical laboratory. Data validation provides a level of assurance, based on a technical evaluation, that an analyte is present or absent and, **if** present, the level of uncertainty associated with the measurement. Analytical data validation for PFAS methods includes a technical review of the laboratory data package specified in the laboratory SOW. Data validation incorporates an evaluation of sample custody, sample handling and preparation, holding times, instrument calibration, instrument performance, batch QC samples (e.g., LCS), the identification and quantitation of target analytes, performance standards (e.g., isotope dilution standards) and the effect QC performance and/or deficiencies have on the quality of analytical sample data.

A data validation report that includes the results of data validation activities must be completed by the data validator for Level III and Level IV data validation requests and takes, as input, the data verification checklist (or equivalent) and the steps in this plan that are listed as "data validation." Data validation requires that personnel performing it have the appropriate level of training and experience to ensure data review and qualification is completed in a reasonable manner and in accordance with industry practices. Professional judgment may be required when performing data validation. When professional judgment is used, resulting in either qualification of data or data left unqualified, the rationale for the selection of this path will be fully documented in the validation report. Documentation will include the following: citations from this plan, other industry standards, and/or the literature demonstrating the reasonableness of the evaluation.

The actions described in this plan must serve as the baseline for incorporation into project data verification/validation activities. Project-specific procedures applying to analytical methods **NOT** covered in this document and must be reviewed and approved prior to use.

Implementation of this plan is expedited through the agreement of work to be performed by an analytical laboratory in the form of a project-specific laboratory SOW. Deliverable requirements specified in the analytical SOW must be consistent with the requirements of this plan and with the basic ordering agreement contract with the laboratory.

The validation SOW must be written consistent with the requirements and specifications of this plan. The validation SOW is prepared by a SMO representative and communicated to the validation organization (for Level III and Level IV validation only).

The validation SOW will include as attachments full copies of the analytical laboratory data package, as well as an electronic data deliverable (EDD) in the form of a Microsoft Excel file. Placement of the data validation qualifier may be assigned by handwriting on the laboratory report form, initialed and dated, or electronically on provided EDDs in the validation code field. **If** data are **NOT** qualified during data validation, **then** an equals sign ("=") shall be entered on the sample result or placed in the validation code field of the provided EDD.

Form CP3-ES-5003-F03, *Data Verification Checklist* (in accordance with CP3-ES-5003, *Quality Assured Data*), must be completed for every sample delivery group (SDG) that undergoes Level II, III, or IV data validation. In addition to the data verification checklist, a data validation report must be completed for every SDG that undergoes Level III or Level IV data validation.

5. PROCEDURE

NOTE: Refer to Appendix A for qualifier descriptions. Refer to Appendix B for qualification guidance due to multiple quality deficiencies. Refer to Appendix C for a listing of relevant equations to use with this plan.

The following is a step-by-step approach to implement analytical data verification and data validation activities. This approach is based on current industry accepted standards. Because changes to methodology and the referenced guidance documents are **NOT** within the verifier's or the validator's control, the data verifier and the data validator should always follow the most current methodology and associated guidance documents referenced throughout this text to perform the review and validation of associated data.

5.1 DATA VALIDATION STRATEGY AND STATEMENT OF WORK DEVELOPMENT

The project team, with input as needed from a quality assurance specialist and/or a representative of the SMO, shall develop a data validation strategy based on inputs identified through the DQO process. The project-specific sampling and analysis plan will define the DQOs and the framework for performing data validation. A SMO representative shall prepare a validation SOW to communicate data verification and validation requirements to the organization performing the work (for Level III and Level IV validation only).

5.2 CUSTODY OF SAMPLES AND SAMPLE DOCUMENTATION

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 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 the sample truly has been in custody from the field to the final result), an evaluation of field notes, 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 is in an authorized person's possession and is 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 true identity of each sample. When custody problems **CANNOT** be resolved, they will affect the defensibility of the sample.

5.2.1 Data Verification

The data verifier shall trace custody of all samples in the reporting batch from field sampling through receipt at the laboratory by reviewing the COCs. **If** the information is missing, **then** the data verifier will seek to obtain field documentation from the sampler or laboratory to determine whether 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, etc.), **then** indicate the problem on the data verification checklist.

5.2.2 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 qualify associated results "R."

5.3 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.

5.3.1 Deliverables

- Field Sampling Notes
- Field COCs
- Laboratory COCs
- Laboratory reports and/or raw data containing the following: dates of collection, preparation, and analysis for all samples, dilutions, and re-extractions.

5.3.2 Criteria

Table 2 provides current industry-accepted standards for sample preservation and holding 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 requirement.

Table 2. Holding Times and Preservation Criteria

Sample Type	Sample Matrix	Container	Preservative	Holding Time
PFAS	Drinking or Potable Waters EPA Method 537.1 (EPA 2020a).	2 × 250-mL polypropylene bottle with polypropylene caps.	0–10°C preserved with Trizma	14 days[a] 28 days[b]
	Nonpotable waters (including leachates) EPA Draft Method 1633.	(3 × 500-mL)[c] high density polyethylene (HDPE) sample bottle with linerless HDPE or polypropylene caps.	0–6°C or frozen ≤ -20°C[d]	28 days[a] 90 days[b]
	Solid samples (e.g., soils, sediments, sludges, ash) EPA Draft Method 1633.	500-mL wide-mouth, HDPE sample jar with linerless HDPE or polypropylene caps.	0–6°C or frozen < -20°C	90 days[a] 90 days[b]

NOTE: Store sample extracts in the dark at less than 0–6 ºC until analyzed. **If** stored in the dark at ≤ 0 ºC, **then** sample extracts may be stored for up to 90 days, with the caveat that issues were observed for some ether sulfonates after 28 days (see Reference 10). These issues may elevate the observed concentrations of the ether sulfonates in the extract over time. Samples may need to be extracted as soon as possible **if** NFDHA is an important analyte. The information presented in this table does **NOT** represent EPA requirements but rather is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times are provided by the lab.

[a] Time from collection of sample to extraction.

[b] Time from extraction to completion of analysis.

[c] In the absence of source-specific information (e.g., historical data) on the levels of PFAS or project-specific requirements, collect at least three aliquots of all aqueous samples to allow sufficient volume for an original whole-volume analysis, a re-extraction and second analysis, and for the determination of percent solids and for pre-screening analysis. That third aliquot may be collected in a smaller sample container (e.g., 250-mL or 125-mL).

[d] When stored at ≤ -20 ºC and protected from the light, samples may be held for up to 90 days.

5.3.3 Data Verification

The data verifier shall verify the presence of the pertinent COC forms in laboratory deliverables. **If** information is missing, **then** the data verifier will seek to obtain field documentation from the sampler

and/or the contract laboratory to determine whether the omission affects sample integrity. Upon receipt, this information will be placed in the data package for delivery to the data validator. **If** missing information **CANNOT** be obtained or reconstructed from field notes, COCs, etc., **then** the data verifier will note omitted information on the data verification checklist as uncorrectable.

5.3.4 Data Validation

5.3.4.1 Holding Times

Review the data verification 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 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 field and/or laboratory 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 checklist (Table 3).

If the elapsed time falls within the prescribed holding time, **then NO** actions will be taken and **NO** qualification assigned. **If** the holding time is exceeded, **then** qualify as follows:

- **If** the holding time is exceeded by a factor of < 2, **then** qualify detects as "J" and nondetects as "UJ."
- **If** the holding time is grossly exceeded by a factor > 2, **then** qualify detects "J" and nondetects as "R."

5.3.4.2 Temperature/ Preservation

Review laboratory receiving records to determine whether 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 (6°C < sample temperature < 10°C), **then** qualify detects as "J" and nondetects as "UJ," indicating the results are estimated.

- **If** sample temperatures upon receipt are > 10°C, **then** the data validator must evaluate the integrity of the reported concentrations and the data may require qualification of "R."

- **If** samples are collected in unapproved sample containers, **then** qualify detects as "J" and nondetects as "UJ," indicating the results are estimated.

Table 3. Holding Times and Preservation Qualification

Holding Times and Sample Preservation	Qualification Guidance	
Validation Step	Detects	Nondetects
Samples extracted and/or analyzed outside appropriate holding time.	J	UJ/R[a]
Samples preserved improperly.	J	UJ/R[b]

[a] Qualify "R" only **if** holding time has been grossly exceeded either on the first analysis or upon reanalysis.
[b] Use professional judgment in qualifying data.

5.4 MASS CALIBRATION

5.4.1 Deliverables

- Contract laboratory program (CLP) form or equivalent for SW-846 methods for each LC/MS/MS system used

- Raw data (required for confirmation)

5.4.2 Frequency

Calibrate the mass scale of the LC/MS/MS with the calibration compounds and procedures prescribed by the manufacturer.

5.4.3 Criteria

The mass calibration must be verified prior to the analysis of any standards and samples and after each subsequent mass calibration. **If** the peak apex has shifted more than approximately 0.2 dalton; **then** recalibrate the mass axis following the manufacturer's instructions.

5.4.4 Data Verification

The data verifier shall verify the presence of required reporting forms. **If** they are **NOT** provided, **then** the data verifier shall contact the laboratory and request that the missing information be provided. **If** the missing information **CANNOT** be provided, **then** the data verifier shall note the omitted information on the data verification checklist as uncorrectable.

5.4.5 Data Validation

The data validator shall review the data verification checklist to confirm the presence of the appropriate forms. **If** the data verification checklist notes that the LC/MS/MS performance forms are missing and these occurrences **CANNOT** be resolved with the contract laboratory, **then** they are considered uncorrectable problems. Place data validation qualification code "P05" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

Mass calibration must be performed at least annually or as recommended by the instrument manufacturer, whichever is more frequent, 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. The mass calibration verification should verify a mass range which includes the ion masses of all target analytes (Table 4).

If the masses differ from their true value by ± 0.2 daltons, **then** qualify detects and nondetects as "R."

Table 4. Mass Calibration Actions for Data Validation

LC/MS/MS Performance Check	Qualification Guidance	
Validation Step	Detects	Nondetects
Masses outside ± 0.2 daltons of true value of the lowest level standard.	R	R

5.5 INITIAL CALIBRATION

Compliance requirements for satisfactory instrument calibration ensure that the instrument is capable of producing acceptable qualitative and quantitative data for all target compounds. The objective of the initial calibration (IC) is to establish a linear range for the native analytes of interest including their respective isotope dilution standard(s) and non-extracted internal standards. The IC is to be used for routine quantitation of samples using the mean relative responses (RRs) and the mean relative response factors (RRFs) established from the calibration.

5.5.1 Deliverables

- CLP Form 6A or equivalent (PFAS IC data)
- Raw data (required for confirmation)

5.5.2 Frequency

IC must be performed before any samples are analyzed for PFAS method analytes. IC also is required **if** any routine continuing calibration does **NOT** meet the required criteria.

5.5.3 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.

Each calibration standard must contain isotope dilution standards and non-extracted internals standards. 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 within the quantitation range. 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.

- **Draft EPA Method 1633:**

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

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

- **EPA Method 537.1:**

  — Validate the IC 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.

All analytes with commercially available stable isotope analogues must be quantified using isotope dilution. Quantitate samples by integrating the total response (i.e., accounting for peaks that are identified as linear and branched isomers) and relying on the IC that uses the linear isomer quantitative standard. **If** a labeled analog is **NOT** commercially available, **then** the extracted internal standard analyte with the closest retention time (RT) or chemical similarity to the analyte must be used for quantitation, as internal standard quantitation, in this case.

Identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine RTs, transitions and transition ion ratios. Target analyte detections should display a signal-to-noise ratio (S/N) of ≥ 10:1 for the quantitative ion and ≥ 3:1 for the confirmation ion, have proper peak integration, and display all ions at the correct RTs with passing ion ratios (50–150%).

If a second-order calibration model is used, **then** one additional concentration is required, with at least six of the seven calibration standards within the quantitation range.

IC must be performed at instrument set-up and after initial calibration verification (ICV) or continuing calibration verification (CCV) failure, prior to sample analysis.

5.5.4 Data Verification

The data verifier shall confirm 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 and shall be identified in this way on the data verification checklist. Place data validation qualification code C07 on the affected data, **if** uncorrectable deliverable deficiencies have occurred. Qualify only **if** the deviation indicates an adverse effect on data quality.

5.5.5 Data Validation

The data validator shall place the following data validation qualification codes **if** the following conditions are met (qualify only **if** the deviation indicates an adverse effect on data quality):

- IC sequence was **NOT** followed, “C03”;
- Appropriate number of standards were **NOT** used, “C24”; or
- Inappropriate concentrations, “C18.”

The data validator shall 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 reporting limit (RL). The laboratory may elect to calculate a linear or quadratic calibration curve. **If** this method is used, **then** there are two options as follows:

- Option 1: linear least squares regression $r^2 \geq 0.995$ or;

- Option 2: nonlinear regression coefficient of determination ≥ 0.99 (6 points shall be used for second order).

Check and recalculate at least one of the %RSD values of the mean and standard deviation of the response factors 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** the %RSD among the calibration point is > 20%, **then** qualify detects as "J" and nondetects as "UJ."
- **If** the r^2 value is < 0.995, **then** qualify detects as "J" and nondetects as "UJ."
- **If** the r^2 value is < 0.99, **then** qualify detects as "J" and nondetects as "R."

If different matrices are included in the same SDG, **then** verify that the correct IC was used with each set of samples of similar matrix.

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 IC 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 RRF and %RSD are found in Appendix C. **If** calculated RRF 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 based on IC alone. Checks must be made for saturation, baseline shift, peak splitting, ion ratios, and other obvious interferences (Table 5).

Table 5. Calibration Actions for Data Validation

Criteria	**Action**	
Validation Step	Detects	Nondetects
IC **NOT** performed.	R	R
IC **NOT** performed at proper frequency.	Professional judgment	Professional judgment
Linearity: r^2 < 0.99.	J	R
Linearity: r^2 < 0.995.	J	UJ
%RSD of calibration points > 20%.	J	UJ
Standard recalculated value outside 70-130% of true value; for standards ≤ RL value outside 50-150% of true value.	Professional judgment	Professional judgment
NOT within appropriate windows and absolute RT of internal standard.	Professional judgment	Professional judgment
If an elimination of either high or low points restore %R < 20%.	J [a]	UJ/R/NA [b]
Positive results do **NOT** exhibit simultaneous peak response for both the quantitation and confirmation ion masses.	J	N/A
S/N < 3:1 in standard for the confirmation ions and S/N < 10:1 for the quantitative ion.	J	N/A

Table 5. Calibration Actions for Data Validation (Continued)

Criteria	Action	
Validation Step	Detects	Nondetects
RT established by midpoint calibration standard or daily CCV. RT changes of +/- 0.4 minutes. For analytes with labeled isotope analogues, analytes must elute within 0.1 minutes of the labeled isotope analogue.	R	
Samples with differing matrices that do **NOT** match IC matrices.	Refer to Section 5.5.5 or the method being reviewed	
Anomalies found in raw data (Level IV validation only).	Refer to Section 5.5.5 or the method being reviewed	
Quantitation ions of 2 compounds are **NOT** at the correct ions for quantitation (Level IV validation).	Refer to Section 5.5.5 or the method being reviewed	
If manual integrations are noted during inspection of raw data (Level IV validation only).	Refer to Section 5.5.5 or the method being reviewed	

[a] Qualify only peaks outside linear portion.
[b] Qualify only **if** the deviation indicates an adverse effect on data quality.

5.6 INITIAL AND CONTINUING CALIBRATION VERIFICATION

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

5.6.1 Deliverables

- CLP Form 7A or equivalent (PFAS calibration check)
- Raw data (required for confirmation)

5.6.2 Frequency

Calibration is verified for PFAS initially following calibration using a second source reference standard and an instrument sensitivity check (lowest level calibration standard equal to or less than RL). An instrument sensitivity check must be analyzed prior to sample analysis. The continuing calibration standard must be analyzed prior to sample analysis and after every ten field samples or less throughout an analytical sequence.

5.6.3 Criteria

The ICV, instrument sensitivity check (ISC), and CCV percent difference (%D) or percent drift for each target analyte and its labeled analogue should be within ± 30%.

The CCV does **NOT** have to be second sourced and should equal a mid-level calibration standard or lowest 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.

5.6.4 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 and shall be identified in this way in the data validation report. Place the data validation qualification code "C07" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

5.6.5 Data Validation

If the %D exceeds ± 30%, **then** qualify detects as "J" and nondetects as "UJ."

For Level IV validation only, conduct raw data confirmation by confirming the quantitation ions of two compounds in the continuing 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 (Table 6).

Table 6. Initial and Continuing Calibration Actions for Data Validation

Criteria	Action	
	Detects	Nondetects
ISC **NOT** analyzed prior to sample analysis.	*	*
%D between initial and continuing calibration points > 30%.	J	UJ
ICV, ISC, and CCV were **NOT** analyzed at the correct frequency.	Professional judgment	

*Qualify only **if** the deviation indicates an adverse effect on data quality.

5.7 BLANKS

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. A preparation blank or method blank (MB) is used to assess the level of contamination 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 or **NOT** there is a systemic problem affecting greater than one sample or whether the contamination is an isolated occurrence.

Additionally, the project team may elect to collect and analyze field and equipment rinsate blanks (ERB) to evaluate the existence and magnitude of contamination that may arise as a result of field level activities.

The field blank (FB) 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.

The ERB provides an indication as to whether or not nondedicated sampling equipment has been properly decontaminated, and what, **if** any, carry over may arise between sampled locations.

The data validation policy for EPA Region 4 has been to evaluate the field and ERB as part of the validation process, but **NOT** to qualify the data based on these field samples.

5.7.1 Deliverables

- CLP Form 4A or equivalent (PFAS MB summary)
- Summary forms of results for all associated blanks
- Raw data (required for confirmation)

5.7.2 Frequency

The instrument blank (IB) for PFAS analysis should be analyzed after the calibration standards and once daily. MBd must be extracted for each 20 samples of similar matrix in each SDG or whenever a sample extraction procedure is performed. The IB should be analyzed after any sample or standard that has saturated ions from a given compound to check for carryover.

5.7.3 Criteria

NO contaminants should be found in any blanks. Reported results must **NOT** be corrected by subtracting blank values.

5.7.4 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. Place data validation qualification code "B07" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

5.7.5 Data Validation

Any compound that is reported in both the blank and sample must be evaluated; however, **if** the same compound is reported in a sample and in more than one blank, **then** the sample shall be evaluated against the blank with the highest concentration of the compound. Sample results must **NOT** be modified by subtracting blank values. When comparing blank results to analytical sample results, ensure that factors such as dilution and different sample weights have been taken into consideration.

- **If** compound is found in a blank but **NOT** an associated sample, **then NO** action is taken.
- **If** the sample concentration is greater than the RL but < 5 × blank concentration, **then** qualify the reported result "U."
- **If** the sample concentration is less than RL and < 5 × blank concentration, **then** qualify the reported result "U."
- **If** sample concentration is greater than RL and > 5 × blank concentration, **then NO** qualification of results is necessary.
- **If** gross contamination (saturated peaks in blank) is present, **then** qualify all affected results as "R."

If an IB is **NOT** analyzed immediately after a sample showing compound(s) at high concentration(s), **then** the data validator must evaluate the analyses following the saturated sample analysis for carryover. Qualify reported compounds significantly affected by instrument carryover as "J" or "R." A summary of these qualifications is included in Table 7.

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 7. Method Blank Qualifications

MBs	Qualification Guidance	
Validation Step	Detects	Nondetects
MBs **NOT** analyzed at the appropriate frequency.	[a]	[a]
Detects > 1/3 of the RL for blanks analyzed by EPA Method 537.1.	[a]	[a]
Sample result greater than RL and > 5 × blank result.	No Qualifications	
Sample result greater than and < 5 × blank result.	U	N/A
Sample result greater than RL and < 5 × blank result.	U	N/A
Gross contamination present in blank.	R	[b]
IB **NOT** analyzed after sample shows high concentrations.	[b]	N/A

[a] Qualify only **if** the deviation indicates an adverse effect on data quality.
[b] Use professional judgment in qualifying data.

5.8 SURROGATE STANDARDS

Surrogate standards are nontarget compounds added to all analytical samples, calibration standards 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 (DOE 2020a). Additionally, isotope dilution standards perform as surrogates.

5.8.1 Deliverables

- CLP Form II or equivalent for SW-846 methods, including surrogate recoveries for all samples, blanks, and QC samples
- Raw data (required for confirmation)

5.8.2 Frequency

Surrogate standards are added to all analytical samples, calibration standards, blanks, and QC samples, as applicable to the method.

5.8.3 Criteria

The surrogate recovery limits must be in the range of 70–130%.

5.8.4 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. Place data validation qualification code "S06" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

5.8.5 Data Validation

- **If** any surrogate %R exceeds the upper control limit, **then** qualify detects as "J" and accept nondetects.
- **If** any surrogate %R is between 10% and the lower control limit, **then** qualify detects as "J" and nondetects as "UJ."
- **If** any surrogate %R < 10%, **then** qualify detects as "J" and nondetects as "R." **If** surrogates are "diluted out," **then** the data validator must use professional judgment to determine whether qualification of data is necessary (Table 8).

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 % recoveries;
- Holding times;
- Comparison of concentration of target compounds; or
- Internal standard areas and RTs.

Table 8. Surrogate Qualifications

Surrogate Standards	Qualification Guidance	
Validation Step	Detects	Nondetects
Surrogate standards **NOT** analyzed at the proper frequency.	*	*
Proper surrogate standards **NOT** used?	*	*
%R > upper control limit.	J	N/A
%R ≥ 10% and < lower control limit.	J	UJ
%R < 10%.	J	R

*Qualify only **if** the deviation indicates an adverse effect on data quality.

5.9 ISOTOPE DILUTION STANDARDS

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. Isotope dilution standard's performance results are critical to the overall accuracy and precision of the analysis since target compound results for each PFAS isomer are quantitated based on the response of the corresponding labeled isomer.

5.9.1 Deliverables

- Recoveries for isotope dilution standards
- Raw data (required for confirmation)

5.9.2 Frequency

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

5.9.3 Criteria

The laboratory performing the analysis will have established acceptance ranges for each isotope dilution standard. In the absence of laboratory limits, the labeled compounds should be within the range of 50–150% recovery of the mid-level calibration standard when a calibration is performed or the initial bracketing CCV.

5.9.4 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. Qualify only **if** the deviation indicates an adverse effect on data quality.

5.9.5 Data Validation

Verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. **If** any criteria have **NOT** been met or **if** information is omitted from the laboratory report, **then** request the missing information from the laboratory. **If** the omission is the result of a technical issue or due to an omitted analytical requirement, **then** a member of the SMO will direct the laboratory to complete the analysis in accordance with the SOW.

The data validator shall check the raw data to verify reported recoveries. Compare the reported %R to the limits appropriate to the method performed (Table 9).

- **If** an isotope dilution standard has a recovery > the upper control limit, **then** qualify detects for the unlabeled analog in that sample as "J."
- **If** an isotope dilution standard has a recovery < the lower control limit, **then** qualify any result for the unlabeled analog in that sample as "J" or "UJ," as appropriate.
- **If** an isotope dilution standard has a recovery < 10%, qualify detects as "J" and any associated nondetects as "R."

Table 9. Isotope Dilution Standards Qualification

Criteria	Qualification Guidance	
Validation Step	Detects	Nondetects
Proper isotope dilution standards **NOT** used.	*	*
Proper internal standard spike concentrations **NOT** used.	*	*
%R is > upper control limit.	J	N/A
%R is < lower control limit.	J	UJ
%R is < 10%.	J	R

*Qualify only if the deviation indicates an adverse effect on data quality.

5.10 NON-EXTRACTED INTERNAL (RECOVERY) STANDARDS

Non-extracted internal standards, also known as recovery 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.

5.10.1 Deliverables

- Percent recovery for recovery (internal) standard
- Raw data (required for confirmation)

5.10.2 Frequency

Non-extracted internal standards are added to all analytical samples, calibration standards, blanks, and quality control samples prior to injection of an aliquot of the extract into the LC/MS/MS.

5.10.3 Criteria

- **Draft EPA Method 1633**

The labeled compounds should be within the laboratory specified acceptance criteria.

- **EPA Method 537.1**

The labeled compounds should be within the range of 70–140% recovery of the most recent CCV, **NOT** to exceed ± 50% from the average area measured during initial analyte calibration (DOE 2020a).

5.10.4 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. Place data validation qualification code "I07" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

5.10.5 Data Validation

The following provides guidance for qualification of samples due to poor internal standard performance. Resulting qualification of compounds is based on results for the associated internal standard.

- **If** peak area %R exceeds the lower limits, **then** qualify detects as "J" and nondetects as "UJ."

- **If** peak area %R exceeds the upper limits, **then** qualify detects as "J" and accept nondetects.

- **If** a performance drop is indicated by extremely low area counts (< 20%), **then** qualify detects as "J" or "R" if the performance drop has significantly affected sample results and nondetects as "R."

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. Qualify false positive results or false negative detection limits with professional judgment as appropriate (Table 10).

Table 10. Recovery Standards Qualification

Recovery (Internal) Standards	Qualification Guidance	
Validation Step	Detects	Nondetects
Samples, blanks, and QC samples **NOT** fortified with recovery (internal) standard spikes?[a]	[b]	[b]
%R for the recovery (internal) standard compounds outside of acceptance criteria?	J	UJ/R[a]
%R for the recovery (internal) standard compounds < 20% of CCV response.	J	R

[a] Qualify as appropriate.
[b] Qualify only **if** the deviation indicates an adverse effect on data quality.

5.11 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

Matrix spike (MS)/matrix spike duplicate (MSD) data are generated to determine long-term precision and accuracy of the analytical method on various matrices. **If** recovery criteria are **NOT** satisfied, there is difficulty in assessing whether the cause was the method or matrix-related interferences. To address this issue, LCSs/ LCSDs also analyzed to verify whether the method results themselves are satisfactory. **If** only the MS/MSD are affected, a matrix effect is likely. Qualification, therefore, is **NOT** applied to sample data based on MS/MSD alone, but is used in conjunction with other QC parameters in judging data usability. Field QC samples (e.g., FB, equipment blank) should **NOT** be used for the MS/MSD. **If** an FB was used for the MS/MSD, this fact should be included in the data validation summary.

NOTE: For a MS that does **NOT** meet the technical criteria, apply the action to all samples of the same matrix, **if** the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and laboratory data for other parameters (e.g., total suspended solids, total dissolved solids, total organic carbon, alkalinity or buffering capacity, reactive sulfide, anions) in determining similarity. The reviewer also should use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the data package. The reviewer 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. Or, the reviewer 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 sample should be qualified.

5.11.1 Deliverables

- CLP 3A or 3B or equivalent (PFAS MS/MSD recovery)
- Raw data (required for confirmation)

5.11.2 Frequency

MS/MSD pairs must be analyzed at a frequency of at least one MS/MSD pair per 20 field samples of similar matrix.

5.11.3 Criteria

The MS/MSD %R should fall within laboratory-determined limits. **If** MS/MSD results fall outside of the laboratory-determined limits, **then** a QC check standard or LCS must be analyzed and fall within those ranges.

5.11.4 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. Place data validation qualification code "M05" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

5.11.5 Data Validation

Verify that the analysis frequency has been satisfied for all instruments used to quantify sample results. If any criteria have **NOT** been met, or **if** information is omitted from the analytical laboratory report, **then** request the missing information from the laboratory. **If** the omission is the result of a technical issue or due to an omitted analytical requirement, **then** a member of the SMO will direct the laboratory to complete the analysis in accordance with the SOW.

A determination shall be made concerning what extent that noncompliant MS/MSD data has on other sample data in regard to the MS/MSD sample 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 sample spiked, 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. MS/MSD data alone shall **NOT** be used exclusively to qualify data, but in conjunction with other supporting QC data. Professional judgment shall be used to determine the need for qualification of reported compounds.

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.

The laboratory also may include a MS/MSD analysis in a data package that is performed on a parent sample and that is **NOT** from the sample set being reviewed. This commonly is called a "batch QC sample." Data validation will **NOT** be made based on batch QC that is generated from a sample that is **NOT** from the data set being reviewed. In this case, the LCS/LCSD will be used to determine the accuracy and precision of the sample set.

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 of data users to fully determine the quality of the reported results. Affected detects shall be qualified as "J" and nondetects as "UJ" unless other quality deficiencies are observed.

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

- **If** MS %R greater than upper control limit, **then** qualify detects as "J." Nondetects do **NOT** require qualification.

- **If** MS %R > 10% and less than lower control limit, **then** qualify detects as "J" and nondetects as "UJ."
- **If** MS %R < 10%, **then** qualify detects as "J" and nondetects as "R."

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

- **If** the relative percent difference (RPD) for water/liquid MS/MSD is > 30%, **then** qualify associated detects as "J" and nondetects should **NOT** be qualified.
- **If** the RPD for soil/solid matrices is > 40%, **then** qualify associated detects as "J" and nondetects should **NOT** be qualified.

Recalculate one MS recovery from raw data for confirmation. Table 11 presents information on MS/MSD qualification. Equation C.1 in Appendix C is used to calculate MS % recovery.

Table 11. MS/MSD Qualification

Criteria	Qualification Guidance	
	Detected Compounds	**Nondetected Compounds**
MS/MSD **NOT** analyzed at the appropriate frequency.	[a]	[a]
%R or RPD greater than upper acceptance limit.	J [b]	**NO** qualification
10% less than %R less than lower acceptance limit.	J [b]	UJ [b]
%R < 10%.	J [b]	R [b]
Lower acceptance limit less than %R less than or equal to upper acceptance limit.	**NO** qualification	

[a] Qualify only **if** the deviation indicates an adverse effect on data quality.
[b] Qualify only after evaluating other QC data in the SDG.

5.12 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.

5.12.1 Deliverables

- CLP Form VI or equivalent for SW-846 methods
- Raw data (required for confirmation)

5.12.2 Frequency

One laboratory duplicate shall 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 (QAPPs, etc.).

5.12.3 Criteria

Samples identified as FBs must **NOT** be analyzed as laboratory duplicate.

For sample concentrations > 5 × RL, the field/laboratory duplicate precision as measured by RPD must be within ± 30% for aqueous samples and 35% for solid matrices. **If** the sample values are < 5 × the RL, **then** RPD does **NOT** apply. Instead, the absolute difference between sample and duplicate must be less than the RL,

5.12.4 Data Verification

The data verifier shall verify that FBs were **NOT** analyzed as laboratory duplicates. **If** an FB has been used, **then** the SMO will be notified immediately to ensure timely corrective action. **If** reanalysis **CANNOT** be completed, **then** this issue will be identified as uncorrectable on the data verification checklist.

The data verifier shall verify the presence of laboratory and field duplicate results (if performed). **If** they are **NOT** provided or **if** the required frequency of analysis is **NOT** demonstrated in the laboratory deliverable, **then** the data verifier will seek to obtain the missing information from the laboratory. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If the missing information **CANNOT** be obtained from the laboratory, **then** they are considered uncorrectable problems. Place data validation qualification code "D05" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality. As they are contract compliance related, all such occurrences shall be communicated to the SMO and to the data validator on the data verification checklist.

5.12.5 Data Validation

- 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.

Laboratory and field duplicate qualification is provided in Table 12.

Table 12. Laboratory and Field Duplicate Qualification

Duplicate Type	Matrix	RPD	Sample Results	Qualification Guidance
Laboratory Duplicate	Aqueous	> 30%	Sample and duplicate > 5 × RL	Qualify results > RL; "J"
	Solid	> 35%		Qualify nondetects; "UJ"
	Aqueous	> 30%	Sample and duplicate < 5 × RL	Absolute difference > RL; "J"
	Solid	> 35%		Absolute difference < RL; **NO** action

Table 12. Laboratory and Field Duplicate Qualification (Continued)

Duplicate Type	Matrix	RPD	Sample Results	Qualification Guidance
Field Duplicate	Aqueous	> 30%	Sample and duplicate > 5 × RL	Qualify results > RL; "J"
	Solid	> 35%		Qualify nondetects; "UJ"
	Aqueous	> 30%	Sample and duplicate < 5 × RL	Absolute difference > RL; "J"
	Solid	> 35%		Absolute difference < RL; **NO** action

*The above control limits are method requirements for matrix-specific duplicate samples. It should be noted that laboratory variability arising from the subsampling of nonhomogeneous matrices is a common occurrence; therefore, for technical review purposes only, regional policy or project DQOs may allow the use of less restrictive criteria (e.g., 35% RPD, 5 × the RL) to be used in assessing nonhomogeneous matrices. When project-specific DQOs mandate broader precision requirements, this information will be provided to the data validators as part of the validation SOW.

5.13 LABORATORY CONTROL SAMPLE

An LCS (QC check standard) is analyzed to provide accuracy of the analytical method.

5.13.1 Deliverables

- LCS recovery form or equivalent
- Raw data (required for confirmation)

5.13.2 Frequency

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

5.13.3 Criteria

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

- **Draft EPA Method 1633**

  If laboratory limits are **NOT** available, **then** the data validator should follow advisory limits from Table 5A in EPA Draft Method 1633 (EPA 2022).

- **EPA Method 537.1**

  Results of the low-level LCS analyses must be 50–150% of the true value. Results of the medium and high-level LCS analyses must be 70–130% of the true value (DOE 2020a).

5.13.4 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. Place data validation qualification code "L05" on the affected data **if** uncorrectable deliverable deficiencies have occurred; qualify only **if** the deviation indicates an adverse effect on data quality.

5.13.5 Data Validation

Confirm that the LCS was prepared and analyzed. The following provides guidance for qualification of samples due to poor LCS performance. Resulting qualification of compounds is based on the number of LCS compounds outside of the laboratory determined limits and the percent recovery of those compounds (Table 13).

- **If** LCS recovery results are greater than acceptance limits, **then** the data validator shall qualify detects as "J." There is **NO** qualification for nondetects.
- **If** LCS recovery results are greater than 10% but less than acceptance limits, **then** the data validator shall qualify detects as "J" and nondetects as "UJ."
- **If** LCS recovery results are < 10%, **then** qualify detects as "J." Nondetects shall be evaluated by the validator and may be qualified as "R."
- **If** an LCSD is included with the analyses, and the calculated %RPD between the LCS and LCSD results exceeds laboratory limits or 30%, **then** qualify associated target analytes as "J."

Table 13. LCS Qualification

Laboratory Control Sample	**Qualification Guidance**	
Validation Step	Detects	Nondetects
LCS was **NOT** analyzed at the proper frequency.	*	*
LCS was **NOT** prepared and analyzed.	*	*
%R of the reported compounds outside of acceptance criteria.	J	UJ
%R or RPD greater than upper acceptance limit.	J	**NO** qualification
10% < %R less than lower acceptance limit.	J	UJ
%R < 10%.	J	R*
LCS was **NOT** same matrix as the analyzed samples.	*	*

*Use professional judgment in qualifying data

5.14 CLEANUP

Cleanup is performed to remove matrix interferences from sample extracts prior to analysis.

5.14.1 Deliverables

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

5.14.2 Frequency

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

5.14.3 Data Verification

Place reason code "V04" on the affected data **if** uncorrectable deliverable deficiencies have occurred.

5.14.4 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.

5.15 REPORTING LIMITS/SAMPLE QUANTITATION LIMITS

RLs have been developed to enable the laboratory to meet realistic detection limit goals. RLs have been determined by EPA to be calculated as 3σ sigma above the method detection limit (MDL).

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).

5.15.1 Deliverables

CLP Form I or equivalent for SW-846 analytical methods for all samples

5.15.2 Frequency

RLs or SQLs are reported for all compounds that are **NOT** detected above the method MDL.

5.15.3 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.

5.15.4 Data Validation

For all samples, the SQL must be less than or equal to RL, which are identified and communicated to the analytical laboratory in the laboratory SOW. **If** the SQL is greater than RL, this may indicate matrix-related problems or analytical conditions precluding RL achievement.

All sample results should be reviewed to determine RL compliance. In cases where the SQL is greater than RL, the project may decide to request a reanalysis.

- Verify that compounds detected at levels below the SQL have been qualified as "J" by the analytical laboratory.

- Verify results for each analyte in each field sample or QC standard were reported at or above the MDL to 3 significant figures. Report a result for each analyte found in each field sample or QC standard below the MDL as "< MDL."

- Verify results for each analyte in a blank were reported at or above the MDL to two significant figures. Report a result for each analyte found in a blank below the MDL as "< MDL."

- Verify results for an analyte found in a sample or extract that has been diluted at the least dilute level at which the area at the quantitation mass to charge (m/z) is within the calibration range and with isotopically labeled compound recoveries within their respective QC acceptance criteria. This may require reporting results for some analytes from different analyses.

For one nondetect compound in each sample blank, verify that RLs have been adjusted for deviation from the nominal preparation and analysis conditions, such as sample size, aliquot, if necessary. **NO** additional validation qualifiers are necessary for results detected below the SQL unless directed in other sections of this plan.

5.16 TARGET COMPOUND IDENTIFICATION AND QUANTITATION

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

5.16.1 Deliverables

- CLP Form I or equivalent (PFAS analysis data sheet)
- Raw data (required for confirmation)

5.16.2 Criteria

For target analytes or labeled compound analogues to be identified, peak responses of the quantitation and confirmation ions must be at least three times the background noise level (S/N 3:1). The quantitation ion must have an S/N ≥ 10:1 **if** there is **NO** confirmation ion.

Target analyte, extracted internal standard (EIS) analyte, and non-extracted internal standard (NIS) analyte RTs must fall within ± 0.4 minutes of the predicted RTs from the midpoint standard of the IC or initial daily calibration verification (CV), 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 IC standard.

5.16.3 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.

5.16.4 Data Validation

The presence/absence and concentration of detected compounds in the samples are reviewed to determine whether or not 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 data package for the noncompliance.

- **If NO** rationale has been provided, **then** the evaluation of the effect on quantitation of detected target compounds shall be made.

- **If** detected target compounds quantified against the incorrect ion are significantly affected, **then** the affected compounds may be qualified as "R."

- **If** the field sample results do **NOT** all meet the criteria stated in Sections 5.16.2, and all sample preparation avenues (e.g., extract cleanup, sample dilution) have been exhausted, **then** qualify detects as "J" and nondetects as "UJ" to 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 had an effect on a compound, such as reporting of false positives or artificially elevating compound levels, **then** the affected data may be qualified as "R."

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 data package, indicate on the laboratory reporting forms which results are the most reliable.

5.17 MANUAL RECALCULATION OF ANALYTICAL RESULTS

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 sample results are produced primarily through software processing and minimal transcription is performed in the laboratory, **then** the data system(s) can be evaluated during an audit or surveillance by performing two different tests on the software. First, supply the data system a consistent set of input designed to provide a consistent set of output. Next, supply the data system a set of nonconforming data to test the error detection routines. An additional evaluation of the laboratory's software configuration control and security is also necessary. Through this technique, a high level of confidence can be gained in the laboratory's reporting techniques and will result in a minimal need for manual recalculation of sample results.

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. Data may be qualified "R" as a last resort, **if NO** actions can reproduce reported values.

Calculations for compound quantitation and rounding rules can be found in Appendix C.

6. RECORDS

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

- Data verification checklist (for Level II, III, and IV validation only)
- Data validation report (for Level III and Level IV validation only)
- Copies of qualified or unqualified results reports (if applicable)

7. REFERENCES

NOTE: Use the most current versions of the references listed below for the data review, verification, and validation process.

DOD (U.S. Department of Defense) 2020. *Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl Substances Analysis* by QSM Table B-15, U.S. Department of Defense Environmental Data Quality Workgroup, Washington, DC, May.

EPA 2020a. *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 2020b. *Contract Laboratory Program National Functional Guidelines for High Resolution Superfund Methods Data Review*, EPA-542-R-20-007, U.S. Environmental Protection Agency, Washington, DC, November.

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 2022. *Analysis of Per- and Polyfluoroalkyl Substances in Aqueous, Solid, Biosolids, and Tissue Samples by LC/MS/MS*; EPA Draft Method 1633; U.S. Environmental Protection Agency Washington, DC, December.

NYSDEC (New York Department of Environmental Conservation) 2023. *Sampling, Analysis, and Assessment of Per-And Polyfluoroalkyl Substances (PFAS)*, New York Department of Environmental Conservation, New York, NY April.

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APPENDIX A

DATA VALIDATION QUALIFIERS AND QUALIFICATION CODES

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DATA VALIDATION QUALIFIERS AND QUALIFICATION CODES

Data Validation Qualifiers

U—Analyte compound or nuclide considered not detected above the reported detection limit.
J—Analyte compound or nuclide identified; the associated numerical value is approximated.
UJ—Analyte compound or nuclide not detected above the reported detection limit, and the reported detection limit is approximated due to quality deficiency.
NJ—Presumptively present at an estimated quantity (use with TICs only).
= – "Equals" sign, indicates that no qualifier is necessary.

Data Validation Qualification Codes

Blanks
B01—Sample concentration was ≤ RDL and < 5 × the blank concentration (10 × for common contaminants).
B02—Sample concentration was > RDL 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 RRF was < 0.05
C02—Initial calibration %RSD was exceeded
C03—Initial calibration sequence was not follows as appropriate
C04—Continuing calibration RRF was < 0.05
C05—Continuing calibration %D was exceeded
C06—Calibration or performance check was not performed at the appropriate frequency
C07—Calibration data not reported
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 RSD criteria were not satisfied
C14—Retention time of compound outside window
C15—Initial calibration % 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—CRI %R was below the lower acceptance limit
C22—CRI %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 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
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 (QC Check Standard)
K01—QC Check Standard not analytically prepared but only analyzed
K02—Recovery of QC Check Standard was above upper control limits
K03—Recovery of QC Check Standard was below lower control limits
K04—QC Check Standard data not analyzed or not reported
K05—Other (describe in comments)

Laboratory Control Sample
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 and MS/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 (PEM) 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—TIC result was not above 10 × the level found in the blank
Q10—TIC reported as detect in another fraction
Q11—Common artifact reported as a TIC
Q12—No raw data were provided to confirm quantitation
Q13—MDA > RDL
Q14—Inappropriate aliquot sizes were used
Q15—Sample result < MD
Q16—Sample result < 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—RT outside calculated RT window
Q28—Neither CRQL or the SQL are reported for a nondetect result
Q29—SQL > RDL
Q30—Compound detected at < 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 hour
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—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 CRQL 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
V05—Cleanup check not performed at the appropriate 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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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 RSD	Quantitation
Continuing Calibration	Quantitation
Method Blank	Positive bias
Internal Standard (Labeled Compound) Spike	Positive or negative bias
Laboratory Control Sample	Method bias
Matrix Spike/Matrix Spike Duplicate	Positive or negative bias and precision
Recovery (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 SOW 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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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 Surrogate Recovery

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

where:
A = calculated SUR concentration for the QC or Field Sample
B = fortified concentration of the SUR

C.2 Percent Recovery

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

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

C.3 For Duplicate Measurements

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

where:
F1 = Result 1
F2 = Result 2

C.4 Mean RR of RRF

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

where:
RR or RRFi = Relative Response or Relative 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:
xi = Nominal concentration (true value) of each calibration standard
x′i = 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 EIS
M_{EIS}= The mass of the EIS added (ng)
RR= Average response ratio used to quantify target compounds by the isotope dilution method
RRF= Average response factor used to quantify target compounds by the extracted internal standard method
Ws= Sample volume (L) or weight (g)

C.9 Concentration of EIS Analyte

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

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

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