CP2-ES-5107/FR2

Inorganic Analyses
Data Verification and Validation for the
Paducah Gaseous Diffusion Plant,
Paducah, Kentucky

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Data Verification and Validation for the
Paducah Gaseous Diffusion Plant,
Paducah, Kentucky

Date Issued—December 2025

U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

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

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APPROVALS

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Approved by:

CALEB KLINE (Affiliate)

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REVISION/CHANGE LOG				
Revision/Change Letter	**Description of Changes**	**Pages Affected**	**Date of Revision/Change**	**Approved By (signature on file)**
FR0	Bluesheet	All	11/14/2017	Signature on file
FR1	Nonintent Change for Bluesheet Incorporation.	All	12/31/2017	Signature on file
FR1A	Nonintent Change to update approver. Updated required review date.	All	7/1/2021	Signature on file
FR1B	Periodic Review has been completed with no changes identified in procedure technical content. Nonintent changes have been incorporated per CP3-NS-2001. Date for review cycle has been reset.	All	10/16/2024	Signature on file
FR2	General revision to update plan according to DoD/DOE QSM 6.0 requirements and other applicable professional guidance to address CA-005369, AI-0008630.	All	12/9/2025	Signature on file

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CONTENTS

TABLES

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ACRONYMS

CCB	continuing calibration blank
CCV	continuing calibration verification
COC	chain-of-custody
CVAA	cold vapor atomic absorption
CVAFS	cold vapor atomic fluorescence spectrometry
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ICS	interference check sample
ICV	initial calibration verification
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
N/A	not applicable
PDS	post-digestion spike
QAPP	quality assurance project plan
QC	quality control
QSM	quality systems manual
RL	reporting limit
RPD	relative percent difference
SAEP	sampling analysis and event plan
SAP	sampling and analysis plan
SDG	sample delivery group
SMO	sample management office
SOW	statement of work
%D	percent difference
%R	percent recovery
%RE	percent relative error
%RSE	percent relative standard error

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DEFINITIONS

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

NOTE 2: In this plan, the words "shall" and "must" are used to denote a requirement; the word "should" 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 affected when it is significantly influenced by a quality deficiency and is qualified accordingly through analytical data validation.

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

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

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

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

Contract-Required Detection Limit— The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is > 0.

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

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

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

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

physical qualification of the data. Data validation occurs prior to drawing a conclusion from the body of data.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1. INTRODUCTION

1.1 PURPOSE AND SCOPE

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

This document focuses on data generated by the following inorganic methods found in aqueous and solid matrices.

- U.S. Environmental Protection Agency (EPA) Method 1631, *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* (CVAFS)
- EPA Method 200.7, *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry* (ICP-AES)
- EPA Method 200.8, *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry* (ICP-MS)
- EPA Method 245.1, *Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry* (CVAA)
- EPA Method 245.2, *Mercury (Automated Cold Vapor Technique) by Atomic Absorption*; CVAA
- SW-846 Method 6010, *Inductively Coupled Plasma-Optical Emission Spectroscopy* (ICP-OES)
- SW-846 Method 6020, *Inductively Coupled Plasma-Mass Spectrometry*; ICP-MS
- SW-846 Method 7470, *Mercury in Liquid Wastes (Manual Cold-Vapor Technique)*; CVAA
- SW-846 Method 7471, *Mercury in Solids or Semisolid Waste (Manual Cold-Vapor Technique)*; CVAA

When applicable, this plan incorporates requirements that are defined in the U.S. Department of Defense (DoD) and U.S. Department of Energy (DOE) Quality Systems Manual (QSM) for Environmental Laboratories Version 6.0; however, data validators should reference the most current version of the DoD/DOE QSM when validating data (DoD and DOE 2023). Data produced by analytical methods for which this plan provides limited guidance may necessitate the development of modified criteria from this plan; however, the general validation strategy outlined in this plan should be applicable. In the absence of specific guidance, data validators are advised to seek guidance in the specific method employed and/or from other industry standards. Examples include the National Functional Guidelines for Inorganic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

1.2 APPLICABILITY

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

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

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

2. RESPONSIBILITIES

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

Table 1. Responsibilities for Data Validator and SMO

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

3. GENERAL INFORMATION

3.1 LEVELS OF LABORATORY DATA DELIVERABLES

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

Table 2. Required Laboratory Report Elements

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
Cover/Signature Page/Executive Summary	✓	✓	✓	✓
Table of Contents	✓	✓	✓	✓
Laboratory Report Narrative	✓	✓	✓	✓
Method Summary		✓	✓	✓
Sample Summary/Sample Data Sheets	✓	✓	✓	✓
Shipping and Receiving Documents	✓	✓	✓	✓
Client Chain-of-Custody (COC)	✓	✓	✓	✓
Sample Receipt Checklist	✓	✓	✓	✓
Interlab COC (where applicable)	✓	✓	✓	✓
Subcontract Laboratory COC (if required)	✓	✓	✓	✓
Glossary of Abbreviations and Laboratory Definitions	✓	✓	✓	✓
Quality Control (QC) Association Summary/Sample Traceability	✓	✓	✓	✓
Analysis Run Log			✓	✓
Surrogate and/or Tracer and Carrier Recovery Report	✓	✓	✓	✓
Method Blank (MB) Reports		✓	✓	✓
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD) Summary		✓	✓	✓
Matrix Spike (MS)/Matrix Spike Duplicate (MSD) Summary		✓	✓	✓
Duplicate Sample Summary		✓	✓	✓
Instrument Performance Check Summary			✓	✓
Calibration Data			✓	✓
Internal Standard Area and Retention Time (RT) Summary			✓	✓
Continuing Calibration [Initial Calibration Verification (ICV)/Continuing Calibration Verification (CCV)] Summary Report			✓	✓
Instrument Blank Report			✓	✓
Detection Limits Summary			✓	✓
Gas Chromatography Dual Column Identification Summary			✓	✓
Linear Ranges			✓	✓
Preparation Batch Log			✓	✓
Interference Check Standard Summary			✓	✓
Serial Dilution Summary			✓	✓
Cleanup Log			✓	✓
Standard/Reagent Traceability Log			✓	✓
Accreditation/Certification Summary			✓	✓
Raw Sample Data			✓	✓
Raw QC Data			✓	✓
Manual Integration Summary			✓	✓

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

3.2 STAGES OF VALIDATION

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

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

Stage 1 Validation: A verification and validation based only on completeness and compliance of sample receipt condition checks. Client sample IDs and target analytes are verified against the COCs for completeness; sample conditions upon arrival at laboratory noted; sample preservation was appropriate and verified by the laboratory; holding times were met; concentrations and units were appropriate; trip blanks, field blanks, equipment rinsate blanks, and field duplicates met the project requirements for frequency and field QC.

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

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

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

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

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

3.3 DATA ASSESSMENT REVIEW

The data assessment review includes the following.

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

The data assessment review is comparable to a Stage 1 and Stage 2A validation (depending on analyte and method). As required by project-specific requirements, a Stage 2B, Stage 3, or Stage 4 validation of the

data package **MAY** be requested. See CP3-ES-5003, *Quality Assured Data*, for more information about the data assessment review process.

3.3.1 Data Verification/Contractual Screen

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

3.3.2 Data Validation

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

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

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

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

3.3.3 Data Assessment

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

3.3.4 Data Usability Assessment

Data usability assessment is the last review step of the data assessment review process prior to release of the data from the project team. Data usability assessment is an integration of all information collected about

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

4. DATA VERIFICATION AND VALIDATION INSTRUCTIONS

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

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

4.1 SAMPLE RECEIPT CONDITIONS

4.1.1 Chain-of-Custody

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

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

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

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

4.1.1.1 Data verification

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

4.1.1.2 Data validation

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

4.1.2 Holding Time, Temperature, and Sample Preservation

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

4.1.2.1 Deliverables

The following are deliverables.

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

4.1.2.2 Criteria

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

Table 3. Holding Time and Sample Preservation Criteria

Parameters	Matrix	Preservatives	Holding Times
All Metals except Mercury	Liquid	pH < 2 with nitric acid	180 days
	Soil, sediment, other solids	None	180 days
Mercury	Liquid	pH < 2 with nitric acid	28 days
	Soil, sediment, other solids	0–6°C	28 days

4.1.2.3 Data verification

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

4.1.2.4 Data validation

Holding Times

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

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

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

- **If** the holding time is exceeded by a factor of < 2, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the holding time is grossly exceeded by a factor of ≥ 2, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

If samples have not been preserved and the holding time has been exceeded, **then** use professional judgment when qualifying the data.

Temperature/Preservation

Review the laboratory receiving records to determine if samples were received at the appropriate temperature and if proper preservative addition occurred. **If** records demonstrate that samples were received by the laboratory at the proper temperature with proper preservation, **then NO** action will be taken and **NO** validation code will be applied.

If sample receipt temperatures are exceeded and/or proper preservation was **NOT** followed, **then** apply validation codes to data as follows.

- **If** sample temperature upon receipt is elevated (6°C < sample temperature ≤ 10°C), **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** sample temperature upon receipt > 10°C, **then** the data validator must evaluate the integrity of the reported concentrations, and the data may require an application of an "R" validation code.

- **If** samples are received at an elevated temperature **and** proper preservation has **NOT** been followed (i.e., pH adjustment), **then** professional judgment should be applied to determine the usability of the data.

- **If** samples have not been preserved properly in the field, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** samples for dissolved metals in water are **NOT** filtered in the field **and** instead are filtered upon arrival at the laboratory, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

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

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

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. Samples analyzed outside the appropriate holding time (< 2× holding time).	J	UJ
2. Samples analyzed outside the appropriate holding time (≥ 2× holding time).	J	R
3. Samples received at elevated temperature (≤ 10°C) with correct preservative (if applicable).	J	UJ
4. Samples received at elevated temperature (> 10°C) with correct preservative (if applicable).	*	*
5. Samples preserved improperly in the field.	J	UJ
6. Dissolved metals samples **NOT** filtered in the field.	J	UJ

*Use professional judgment.

4.2 SAMPLE-RELATED QUALITY CONTROL RESULTS

4.2.1 Blanks

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. All blanks should be processed using same sample preparation and cleanup steps applicable to the analytical method. It has been the EPA Region 4 data validation policy to evaluate trip blanks, field blanks, and equipment rinsate blanks as part of the validation process, but not to apply validation codes to the data based on field sample results.

Instrument Blank

Initial calibration blanks and continuing calibration blanks (CCBs) are used to ensure a stable instrument baseline before analysis of analytical samples.

Method Blank

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

Field Blank

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

Equipment Rinsate Blank

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

4.2.1.1 Deliverables

The following are deliverables.

- MB report for each MB
- Instrument blank report
- Raw data (required for confirmation)

4.2.1.2 Frequency

The MB should be analyzed at a frequency of one per batch of 20 samples or less. The MB **must** be similar matrix in each SDG **and** prepared the same as the associated samples. **If** required by the analytical method, **then** instrument blanks are analyzed following initial calibration **and** at a frequency established by the method throughout the analytical run to follow CCVs.

4.2.1.3 Criteria

A blank **shall** be considered contaminated **if** one of the following occurs:

- the concentration of any target analyte in the blank exceeds one-half of the reporting limit (RL) or one-tenth the amount measured in any associated sample, whichever is greater.

- the concentration of any target analyte identified as a common laboratory contaminant in the blank exceeds the RL or one-tenth the amount measured in any associated samples, whichever is greater.

4.2.1.4 Data verification

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

4.2.1.5 Data validation

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

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

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

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

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

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

- **If** sample concentration is greater than the RL and > 5× blank concentration, **then** no qualification of the data is necessary.
- **If** sample concentration is greater than RL and ≤ 5× blank concentration, t**hen** apply a "J" validation code to detected results.
- **If** both blank concentration and sample concentration are greater than the MDL and less than or equal to RL, **then** apply a "U" validation code to detected results.
- **If** gross contamination is present, **then** apply an "R" validation code to detected results.

If an instrument blank is **NOT** analyzed immediately after a sample showing analyte(s) at high concentration(s), **then** the data validator must evaluate the analyses following the saturated sample analysis for carryover. Apply a "J" validation code to reported analytes significantly affected by instrument carryover.

For Stage 4 validation only, conduct the raw data confirmation by determining from raw data whether compounds reported in the blanks are detected above the MDL.

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

Table 5. Blanks Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. Blanks **NOT** analyzed.	R	Not applicable (N/A)
2. Blanks **NOT** the same matrix as the samples.	R	N/A
3. Sample result greater than RL and > 5× blank result.	N/A	N/A
4. Sample result greater than RL and ≤ 5× blank result.	J	N/A
5. Sample and blank result > MDL and ≤ RL.	U	N/A
6. Gross contamination.	R*	N/A
7. Instrument blank **NOT** analyzed after sample shows high concentration.	J*	N/A

*Use professional judgment in qualifying data.

4.2.2 Laboratory Control Sample/Laboratory Control Sample Duplicate

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

4.2.2.1 Deliverables

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

4.2.2.2 Frequency

The LCS **shall** be prepared **and** analyzed with each analytical batch to demonstrate proficiency of the analytical method. Typically, an LCS is prepared and analyzed with each analytical batch of samples requiring sample preparation (i.e., digestion, extraction) before analysis.

4.2.2.3 Criteria

The LCS **must** be analyzed and the LCS %R **must** fall within the DoD/DOE QSM limits. **If** DoD/DOE QSM limits are not available, **then** limits specified by the analytical method or the laboratory should be used. It is recommended that the LCS be the same matrix as the analytical samples. Unless prepared with the analytical samples, the LCS will **NOT** provide a representation of method accuracy. The LCS is prepared from the addition of an LCS concentrate into the appropriate clean matrix and analyzed. All reported analytes **must** be spiked in the LCS and LCSD (if applicable).

In rare cases, a matrix-specific LCS may not be available. In such cases, an LCS of similar matrix will be selected and analyzed. In absence of a similar matrix, an aqueous LCS may be used by the laboratory. The data validator should make a note if an aqueous LCS was used with solid field samples. **If** an aqueous LCS used for soil samples is out of %R criteria, **then** careful inspection must be made to determine the effect(s) on sample data. In comparing an aqueous LCS to soil sample data, ensure that units are comparable.

Review reported LCS results versus raw data (if provided) to ensure accuracy in the values. Recalculate 5% of reported LCS results to verify laboratory calculations (Stage 3 and 4 validations only).

4.2.2.4 Data Verification

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

4.2.2.5 Data Validation

If the LCS criteria are not met, **then** laboratory performance and method accuracy are in question. The data validator **shall** verify that the LCS and/or LCSD were prepared and analyzed in the same fashion as the sample they accompany. Qualification should be applied only if the LCS and other QC data within the batch indicate that the accuracy of reported analytes have been affected. Professional judgment should be used to determine if the data should be qualified. The following guidance is suggested for qualifying sample data for which the associated LCS and/or LCSD does not meet the required criteria.

- **If** an LCS was **NOT** analyzed with the analytical batch, **then** apply an "R" validation code to detected and nondetected results.

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

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

- **If** the LCS %R for an analyte is ≥ 20% **and** less than the DoD/DOE QSM lower acceptance limit, **then** apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.

- **If** the LCS %R for an analyte < 20%, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

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

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

NOTE: In the event poor LCS recoveries are observed for antimony and silver, data validators are advised to evaluate results for both elements knowing that both antimony and silver traditionally are very difficult to recover from solid matrices. In most cases, it is prudent to qualify antimony and silver results "J" estimated based on poor LCS recoveries, unless other QC difficulties are observed in conjunction with poor LCS performance.

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

Table 6. LCS Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. LCS **NOT** prepared and analyzed.	R	R
2. LCS NOT analyzed at the proper frequency.	J	UJ
3. LCS %R > DoD/DOE QSM upper acceptance limit.	J	N/A
4. LCS %R ≥ 20% and < DoD/DOE QSM lower acceptance limit.	J	UJ
5. LCS %R < 20%.	J	R
6. LCS and LCSD RPD > 30%.	J	N/A
7. Analyte **NOT** spiked in LCS/LCSD.	R	R

4.2.3 Matrix Spike/Matrix Spike Duplicate

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

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

4.2.3.1 Deliverables

The following are deliverables for evaluating MS/MSD.

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

4.2.3.2 Frequency

MS/MSD are analyzed at a frequency of once per 20 samples of similar matrix and concurrently with the samples in the SDG, unless a MS/MSD analysis is **NOT** required. A post-digestion spike (PDS) **shall** be performed for any analyte (excluding silver) **if** the MS or MSD fails.

4.2.3.3 Criteria

The MS/MSD %R should fall within DoD/DOE QSM limits. In the absence of DoD/DOE QSM limits, MS/MSD %R shall be evaluated against the laboratory-defined limits. **If** the MS/MSD results fall outside the acceptance limits, **then** a PDS will be performed to evaluate the matrix effect. The LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. The full target analyte list **must** be spiked in the MS/MSD pair(s).

- **If** sample concentration is > 4× the added spike concentration in the MS/MSD, **then** the MS/MSD %R criteria are **NOT** applicable.

- **If** the MS and/or MSD %R is **NOT** within DoD/DOE QSM limits **and** a PDS is analyzed, **then** the PDS %R should fall within DoD/DOE QSM limits.

- **If** an MS/MSD pair is analyzed, **then** the RPD for an MS/MSD pair should be ≤ 20%.

4.2.3.4 Data verification

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

4.2.3.5 Data validation

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

If MS/MSD analysis was required, but **NOT** performed, **then** qualify data 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/LCSD pair as a substitute to provide an evaluation of accuracy and precision in the measurable range of the method.

In the absence of either the MS/MSD, PDS, or LCS/LCSD, it is unlikely that a complete evaluation of method precision and accuracy can be completed. In this case, at a minimum, sample results should be considered estimated quantities due to the inability to fully determine the quality of the reported results. **If** an MS/MSD was **NOT** analyzed, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results unless other quality deficiencies are observed.

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

A determination shall be made concerning what extent the noncompliant MS/MSD recoveries have on other sample data regarding the sample matrix effect itself, as well as specific compounds in samples associated with the MS/MSD. In those instances where it can be determined that the results of the MS/MSD affect only the parent sample, then application of validation codes 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.

For raw data confirmation, recalculate one MS recovery from raw data. See Appendix C for calculation for MS %R (Stages 3 and 4 data validation only).

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

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

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

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

- **If** the MS %R for an analyte is ≥ 30% **and** less than the DoD/DOE QSM lower acceptance limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** the MS %R for an analyte is < 30% **and** the PDS %R is within the DoD/DOE QSM acceptance limits, **then** apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.

- **If** the MS %R for an analyte is < 30% **and** the PDS %R is less than the DoD/DOE QSM lower acceptance limit, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

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

- **If** the RPD for MS/MSD pair > 20%, then apply a "J" validation code to detected target analytes. No qualification is necessary for nondetected results.

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

Table 7. MS/MSD Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. MS/MSD **NOT** analyzed.	J*	UJ*
2. Analyte **NOT** spiked in MS/MSD.	R	R
3. MS %R outside acceptance limits and sample concentration > 4× spiked amount.	N/A	N/A
4. MS %R > DoD/DOE QSM upper acceptance limit.	J	N/A
5. MS %R ≥ 30% and < DoD/DOE QSM lower acceptance limit.	J	UJ
6. MS %R < 30% and PDS %R within DoD/DOE QSM acceptance limits.	J	UJ
7. MS %R < 30% and PDS %R < DoD/DOE QSM lower acceptance limit.	J	R
8. MS/MSD RPD > 20%.	J	N/A

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

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

4.2.4 Duplicates

A laboratory duplicate sample may be 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 homogeneous, and most soil/sediment samples are homogeneous within a factor of two or three.

4.2.4.1 Deliverables

The following are deliverables for evaluating duplicates.

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

4.2.4.2 Frequency

If analyzed, laboratory duplicates 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.).

4.2.4.3 Criteria

The following are criteria for laboratory and field duplicates.

- Samples identified as field blanks or equipment rinsate blanks must **NOT** be analyzed as the laboratory duplicate.
- For sample concentrations > 5× the RL, the RPD precision criteria for aqueous and solid laboratory duplicate samples must be within ± 20%.
- For sample concentrations > 5× the RL, the RPD precision criteria for aqueous field duplicate samples must be within ± 25%. The RPD precision criteria for solid field duplicate samples must be within ± 40%.
- **If** the sample results < 5× the RL, **then** RPD does not apply. Instead, the absolute difference between the sample and duplicate results must be less than the RL.

4.2.4.4 Data Verification

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

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

4.2.4.5 Data Validation

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

- Examine the raw data (if provided) for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility).
- Verify that appropriate methods and amounts were used in preparing the samples for analysis.
- Verify that there are no transcriptions or reduction errors (e.g., dilutions, percent solids, sample weights) on one or more samples.
- Verify that results fall within the linear range(s) of the instrument, if applicable.

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

- For aqueous and solid matrix laboratory duplicates where sample concentrations ≥ 5× the RL and the RPD between sample and laboratory duplicate > 20%, apply a “J” validation code to detected results and apply an “UJ” validation code to nondetected results.

- For aqueous matrix field duplicates where sample concentrations ≥ 5× the RL and the RPD between sample and field duplicate > 25%, apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.

- For solid matrix field duplicates where sample concentrations ≥ 5× the RL and the RPD between sample and field duplicate > 40%, apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.

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

Table 8 summarizes data validation qualification guidance for issues with the laboratory and/or field duplicate.

Table 8. Laboratory and Field Duplicate Validation Qualification Guidance

Duplicate Type	Matrix	RPD	Sample Results	Validation Qualification Guidance	
				Detects	Nondetects
Laboratory Duplicate	Aqueous	> 20%	Sample and duplicate ≥ 5× RL	J	UJ
	Solid	> 20%			
	Aqueous	N/A (Absolute difference greater than RL)	Sample and duplicate < 5× RL	J	N/A
	Solid				
Field Duplicate	Aqueous	> 25%	Sample and duplicate ≥ 5× RL	J	UJ
	Solid	> 40%			
	Aqueous	N/A (Absolute difference greater than RL)	Sample and duplicate < 5× RL	J	N/A
	Solid				

NOTE: 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., 25% 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.

4.2.5 Serial Dilution Analysis

Serial dilution (SD) analysis determines whether significant physical or chemical interferences from the MS are present and are affecting the analysis of samples. This five-fold dilution is prepared from a selected digested sample. SD is only applicable for ICP methods.

4.2.5.1 Deliverables

The following are deliverables for evaluating serial dilutions.

- Serial Dilution Summary Forms
- Raw data (required for confirmation)

4.2.5.2 Frequency

An ICP SD analysis **shall** be performed on a sample from each group of samples with a similar matrix type (e.g., water or soil) **or** for each SDG, whichever is more frequent.

4.2.5.3 Criteria

- Field blanks, equipment rinsate blanks, and preparation blanks **must NOT** be used for the SD analysis.
- **If** analyte concentration is > 50× method detection limit (MDL), **then** the SD percent difference (%D) **must** agree within 20% of the original analysis.

NOTE: The above criteria are method requirements for SD samples, regardless of the sample matrix type; however, for technical review purposes only, project DQOs may allow the use of less restrictive criteria (e.g., %D < 25%) to be assessed against serial dilution soil samples.

4.2.5.4 Data Verification

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

4.2.5.5 Data Validation

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

Review reported SD result and compare to raw data to ensure accuracy of reported values. Recalculate 5% of reported SD %D value to verify laboratory calculations. See Appendix C for SD %D calculation equation.

If negative interference is observed in SD analysis (i.e., results of diluted samples are higher than the original sample), **then** use professional judgment in qualifying data.

The following guidance shall be used for evaluating SD analysis.

- **If** the SD %D ≤ 20%, **then** no qualification is necessary.
- **If** the SD %D > 20% **and** the undiluted sample result < 50× the MDL, **then NO** qualification of results is necessary.
- **If** the SD %D > 20% **and** the undiluted sample result ≥ 50× the MDL, **then** apply a "J" validation code to detected results and a "UJ" validation code to nondetected results.

Table 9 summarizes data validation qualification guidance for issues with the SD analysis.

Table 9. SD Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. SD %D ≤ 20%.	N/A	N/A
2. SD %D > 20% and undiluted sample result < 50× the MDL.	N/A	N/A
3. SD %D > 20% and undiluted sample result ≥ 50× the MDL.	J	UJ

4.2.6 Internal Standards

The analysis of internal standards determines the existence and magnitude of instrument drift and physical interferences and is applicable for ICP-MS analyses only. The criteria for evaluation of internal standard results apply to all analytical and QC samples analyzed during the run, beginning with the calibration.

4.2.6.1 Deliverable

The following are deliverables for evaluating internal standards.

- Internal standard summary forms
- Raw data (required for confirmation)

4.2.6.2 Frequency

All samples analyzed during a run **shall** contain internal standards. One or more of the following internal standards **shall** be added to each sample: indium (In), lithium (the ^{6}Li isotope), scandium (Sc), yttrium (Y), rhodium (Rh), terbium (Tb), holmium (Ho), and/or bismuth (Bi). **If** the laboratory uses lithium as an internal standard, the laboratory shall use an ^{6}Li-enriched standard. The laboratory **shall** monitor the same internal standards throughout the entire analytical run **and shall** assign each analyte to at least one internal standard.

4.2.6.3 Criteria

The intensity of the internal standard response in a sample is monitored and compared to the intensity of the response for that internal standard in the calibration blank. The percent relative intensity (%RI) in the sample **shall** fall within 30–120% of the response in the calibration blank.

If the internal standard %RI in the sample falls outside of these limits, **then** the laboratory **shall** reanalyze the original sample at a two-fold dilution with the internal standard added.

4.2.6.4 Data Verification

Verify the presence of ICP-MS internal standards results. **If** they are not provided **or if** the required frequency of analysis is not demonstrated in the laboratory deliverable, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem **and shall** be identified as such on the data verification/validation checklist.

4.2.6.5 Data Validation

NOTE: Apply the action to the affected analytes for each sample that does not meet the internal standard criteria.

The following guidance shall be used for evaluating internal standards.

- **If NO** internal standards were added to a sample, **then** apply an "R" validation code to all results for that sample.
- **If** a target analyte(s) is **NOT** associated to an internal standard, **then** apply an "R" validation code to that target analyte result.
- **If** the internal standard %RIs in a sample are within the 60–125%, **then** no qualification is necessary.
- **If** the internal standard %RI in a sample is **NOT** within 60–125%, **then** apply a "J" validation code to detected results and a "UJ" validation code to nondetected results.

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

Table 10. Internal Standards Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. **NO** internal standards added to sample.	R	R
2. Analyte **NOT** associated with an internal standard.	R	R
3. Internal standard %RI is within 60–125%.	N/A	N/A
4. Internal standard %RI is **NOT** within 60–125%.	J	UJ

4.3 INSTRUMENT-RELATED QUALITY CONTROL RESULTS

4.3.1 Initial Calibration

Compliance requirements for satisfactory instrument calibration ensure that the instrument can produce acceptable qualitative and quantitative data for inorganic analysis methods. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run.

4.3.1.1 Deliverables

The following are deliverables for evaluating initial calibration.

- Initial calibration summary
- Raw data (required for confirmation

4.3.1.2 Frequency

Initial calibration **must** be performed prior to sample analysis.

4.3.1.3 Criteria

ICP-AES, ICP-OES, and ICP-MS Analysis

If a single-level calibration is used, **then** a minimum one high standard and a calibration blank must be included. **If** a multi-level calibration is used, **then** at least one and up to five standards and a blank must be included when evaluating with a linear regression. Six standards and a calibration blank must be included when evaluating with a quadratic regression.

- Single-level calibration **shall** be evaluated for relative error by determination of the percent relative error (%RE) at or near the mid-range of the initial calibration **and** at the low level of the initial calibration (less than or equal to the RL). The maximum allowable %RE at or near the mid-range of the initial calibration **and** low level of the initial calibration **shall** be 10% and 20%, respectively.

- Multilevel calibration **shall** be evaluated for relative error either by determination of the percent relative standard error (%RSE) across all initial calibration levels **or** by determination of the %RE at or near the mid-range of the initial calibration **and** at the low level of the initial calibration (less than or equal to the RL). The maximum allowable %RSE **shall** be 20%. The maximum allowable %RE at or near the mid-range of the initial calibration **and** low level of the initial calibration **shall** be 10% and 20%, respectively. The coefficient of determination (r^2) **must** be ≥ 0.99 for linear and quadratic regressions.

- For ICP-MS analysis only, the mass spectrometer **must** be tuned properly, calibrated for, **and** checked for resolution in the mass regions of interest. Mass spectrometer tuning **must** meet manufacturer's recommendations **and** DoD/DOE QSM tuning acceptance criteria (mass calibration < 0.1 Dalton from the true value; resolution < 0.9 Dalton full width at 10% peak height). Once proper performance has been demonstrated, at least one standard and a blank **must** be analyzed to develop the calibration curve.

CVAA and CVAFS Analysis

- Five standards and a blank **must** be analyzed. r^2 **must** be ≥ 0.99.

4.3.1.4 Data Verification

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

4.3.1.5 Data Validation

Verify that sample results were quantified within the linear range of the instrument and that the calibration standards bracket sample concentrations.

The following is data validation qualification guidance for issues related to the initial calibration.

- **If** the initial calibration has **NOT** been performed, **then** apply an "R" validation code to all associated results.

- **If** a concentration in a sample exceeds the calibration range, **then** the sample **must** be diluted to fall within the calibration range of the instrument. **If** the sample concentration is reported above the calibration range, **then** apply a "J" validation code to the detected results.

- **If** $r^2 \geq 0.90$ **and** $r^2 < 0.99$, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** $r^2 < 0.90$, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

- **If** %RE > 10% near the mid-range of the initial calibration **or** %RE > 20% at the low level of the initial calibration, **then** apply a "J" validation code to detected results and a "UJ" validation code to nondetected results.

- **If** %RSE > 20%, **then** apply a "J" validation code to detected results and a "UJ" validation code to nondetected results.

- **If** the ICP-MS tuning acceptance criteria is **NOT** met, **then** apply an "R" to all results.

Table 11 summarizes data validation qualification guidance for issues with the initial calibration.

Table 11. Initial Calibration Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. Initial calibration **NOT** performed.	R	R
2. Sample exceeds the calibration range and **NOT** diluted/reanalyzed.	J	N/A
3. $r^2 \geq 0.90$ **and** $r^2 < 0.99$.	J	UJ
4. $r^2 < 0.90$.	J	R
5. %RE > 10% (mid-range) or %RE > 20% (low level).	J	UJ
6. %RSE > 20%.	J	UJ
7. ICP-MS tuning acceptance criteria **NOT** met.	R	R

4.3.2 Initial and Continuing Calibration Verification

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

4.3.2.1 Deliverables

The following are deliverables for evaluating ICVs and CCVs.

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

4.3.2.2 Frequency

An ICV **must** be analyzed after the initial calibration. A CCV **must** be analyzed prior to sample analysis **and** after each group of 10 field samples. An opening CCV is **NOT** required **if** samples are analyzed immediately following an ICV.

4.3.2.3 Criteria

The %R for a target analyte in the ICV and CCV analysis will be within 90–110% for mid-level verification. The %R for a target analyte in the ICV and CCV analysis will be within 80–120% for low level verification.

4.3.2.4 Data Verification

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

4.3.2.5 Data Validation

Review the %R in ICV and CCVs and ensure that proper frequency was met.

If the ICV is **NOT** analyzed after an initial calibration or prior to sample analysis, **then** apply an "R" validation code to detected and nondetected results.

If the CCV is **NOT** analyzed prior to or at the end of sample analysis **and** is required, **then** apply an "R" validation code to detected and nondetected results.

The following is data validation qualification guidance for issues related to ICV/CCV when an analyte's %R is outside the acceptance criteria.

Mid-level verification

- **If** the ICV/CCV %R is < 75% for a target analyte, **then** apply an "R" validation code to detected and nondetected results.
- **If** the ICV/CCV %R is ≥ 75% and %R < 90% for a target analyte, **then** apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.
- **If** the ICV/CCV %R is > 110% and %R ≤ 125% for a target analyte, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.
- **If** the ICV/CCV %R is > 125% for a target analyte, **then** apply an "R" validation code to detected results. No qualification is necessary for nondetected results.

Low level verification

- **If** the ICV/CCV %R is < 65% for a target analyte, **then** apply an "R" validation code to detected and nondetected results.
- **If** the ICV/CCV %R is ≥ 65% and %R < 80% for a target analyte, **then** apply a "J" validation code to detected results and apply an "UJ" validation code to nondetected results.
- **If** the ICV/CCV %R is > 120% and %R ≤ 135% for a target analyte, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.
- **If** the ICV/CCV %R is > 135% for a target analyte, **then** apply an "R" validation code to detected results. No qualification is necessary for nondetected results.

Table 12 summarizes data validation qualification guidance for issues with the ICV/CCV.

Table 12. ICV/CCV Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. ICV **NOT** analyzed after initial calibration and prior to sample analysis.	R	R
2. CCV **NOT** analyzed prior to or at the end of sample analysis (if required).	R	R
3. Mid-level: ICV/CCV %R < 75%.	R	R
4. Mid-level: ICV/CCV %R ≥ 75 and %R < 90%.	J	UJ
5. Mid-level: ICV/CCV %R > 110% and %R ≤ 125%.	J	N/A
6. Mid-level: ICV/CCV %R > 125%.	R	N/A
7. Low level: ICV/CCV %R < 65%.	R	R
8. Low level: ICV/CCV %R ≥ 65% and %R < 80%.	J	UJ
9. Low level: ICV/CCV %R > 120% and %R ≤ 135%.	J	N/A
10. Low level: ICV/CCV %R > 135%.	R	N/A

4.3.3 Interference Check Sample

The interference check sample (ICS) verifies the analytical instrument's ability to overcome interferences typical of those found in samples. It is required for all ICP methods only. The laboratory should have analyzed and reported ICS results for all elements being reported from the analytical run and for all interferents (target and nontarget) for those reported elements.

The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A, for all wavelengths used for each analyte reported.

4.3.3.1 Deliverables

The following are deliverables for evaluating ICS.

- ICS summary report
- Raw data (required for confirmation)

4.3.3.2 Frequency

An ICS **must** be run at the beginning of each sample analysis run. The ICS is **NOT** to be run prior to the ICV **and** is to be followed immediately by a CCV, which will then be followed by a CCB.

4.3.3.3 Criteria

ICS Solution A %R **must** fall within 80–120%. The absolute value of the concentration for all nonspiked analytes **must** be less than one-half the RL for ICP-AES and ICP-OES analyses or < 2× the RL for ICP-MS analysis (unless nonspiked analyte is a verified trace impurity from one of the spiked analytes).

ICS Solution AB %R **must** fall within 80–120% of the true value for the analytes and interferents.

4.3.3.4 Data verification

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

4.3.3.4 Data validation

If ICS analysis has **NOT** been performed, **then** apply a "R" validation code to detected and nondetected results.

ICS Solution A and ICS Solution AB

Review the raw data and recalculate 5% of ICS Solution A and Solution AB reported values to ensure results are correct. Determine **if** %Rs are within 80–120% for both ICS Solution A and ICS Solution AB criteria. The following guidance is used for qualifying data when ICS %Rs are outside acceptance criteria.

- **If** the ICS %R for an analyte is > 120%, then apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

- **If** the ICS %R for an analyte is ≥ 50% and < 80%, **then** apply a "J" validation code to detected results and a "UJ" validation to nondetected results.

- **If** the ICS %R for an analyte is < 50%, **then** apply an "J" validation code to detected results and an "R" validation code to nondetected results.

ICS Solution A

The raw data may **NOT** contain results for interferents. In this case, the data validator shall use professional judgment to qualify the data. When raw data contains results for interferents, then the following guidance is used for qualifying data outside acceptance criteria.

- **If** the absolute value of the concentration for a nonspiked analyte is greater than one-half the RL for ICP-AES and ICP-OES analyses, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

- **If** the absolute value of the concentration for a nonspiked analyte is > 2× the RL for ICP-MS analysis, **then** apply a "J" validation code to detected results. No qualification is necessary for nondetected results.

- **If** negative results are observed in the ICS Solution A **and** sample results are < 10× the absolute value of ICS Solution A result, **then** apply a "J" validation code to detected results and a "UJ" validation code to nondetected results.

Actions regarding the interpretation and/or the subsequent qualification of ICP data due to the ICS analytical results can be extremely complex. Use professional judgment to determine the need for the associated sample data to be qualified. The data validator may need to obtain additional information from the laboratory. All interpretive situations then should be recorded in the data validation report.

Table 13 summarizes data validation qualification guidance for issues with the ICS.

Table 13. ICS Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	Nondetects
1. ICS analysis **NOT** performed.	R	R
2. ICS Solution A & AB: %R > 120%.	J	N/A
3. ICS Solution A & AB: %R ≥ 50% and %R < 80%.	J	UJ
4. ICS Solution A & AB: %R < 50%.	J	R
5. ICS Solution A: Absolute value > ½ RL for ICP-AES and ICP-OES.	J	N/A
6. ICS Solution A: Absolute value > 2× RL for ICP-MS.	J	N/A
7. ICS Solution A: Negative result in ICSA and sample result < 10× the absolute value of ICSA result.	J	UJ

4.4 RECALCULATION CHECKS

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

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

NOTE: Calculations for rounding rules can be found in Appendix C.

4.4.1 Reporting Limits/Sample Quantitation Limits

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

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

4.4.2 Deliverables

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

- Sample summary/sample data sheets

4.4.3 Frequency

RLs or SQLs are reported for all analytes.

4.4.4 Data Verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to request they be provided by the laboratory. **If** the missing information cannot be provided by the laboratory, **then** a noncorrectable problem exists.

4.4.5 Data Validation

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

5. RECORDS

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

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

6. REFERENCES

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

CP3-ES-5003, *Quality Assured Data*

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

EPA (U.S. Environmental Protection Agency) 2018. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium*, SW-846, Revisions through Update VI, U.S. Environmental Protection Agency, Washington, DC, December.

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APPENDIX A

DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

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

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

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

NJ Presumptively present at an estimated quantity (use with TICS only)

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

R Result rejected by validator

= Validated result, no additional qualifier necessary

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

Data Validation Reason Codes

Blanks

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

Calibration

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

Calibration (continued)

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

Laboratory Duplicate/Dual Column Sample Confirmation

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

Evidentiary Concerns

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

Interference Check Samples (ICS)

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

General

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

Holding Times/Preservation

H01 Extraction holding times were exceeded
H02 Extraction holding times were grossly exceeded
H03 Analysis holding times were exceeded
H04 Analysis holding times were grossly exceeded
H05 Samples were not preserved properly
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 were exhibited by a major drop-off
I04 Internal standard retention time varied by more than 30 seconds
I05 Inappropriate internal standard used
I06 Inappropriate internal standard concentration(s) used
I07 Internal standard data not reported
I08 Other (describe in comments)

Laboratory Control Sample (LCS)

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

Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

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

Instrument Performance

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

Quantitation

Q01 Peak misidentified
Q02 Target analyte affected by interfering peak
Q03 Qualitative criteria were not satisfied
Q04 Cross-contamination occurred
Q07 Analysis occurred outside 12-hour gas chromatography/mass spectrometry window
Q09 Tentatively identified compound (TIC) result was not above 10 × the level found in the blank
Q10 TIC reported as detect in another fraction
Q11 Common artifact reported as a TIC
Q12 No raw data were provided to confirm quantitation
Q13 Minimum detectable activity (MDA) greater than RL
Q14 Inappropriate aliquot sizes were used
Q15 Sample result less than MDA

Quantitation (continued)
Q16 Sample result less than 2σ uncertainty
Q17 Negative result
Q18 Compounds were not adequately resolved
Q19 Sample geometry different from calibration geometry
Q20 Sample weight greater than greatest weight on mass attenuation curve
Q21 Isotopes of same radionuclide do not show equilibrium
Q22 Peak not within appropriate energy range
Q23 Counting uncertainty ≥ 80% of sample result
Q24 Raw data anomaly
Q25 Other (describe in comments)
Q26 Retention Time (RT) outside calculated RT window
Q28 Neither RL nor the sample quantitation limit (SQL) are reported for a nondetect result
Q29 SQL greater than RL
Q30 Compound detected at less than SQL and not qualified "J"
Q31 Presence of high molecular weight contaminants impacted sample quantitation

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

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

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

Cleanup
V01 10% recovery or less was obtained during either check
V02 Recoveries during either check were > 120%
V04 Cleanup data not reported
V05 Cleanup check not performed at the appropriated frequency
V06 Other (describe in comments)

Dilutions

X01 Serial dilution not analyzed at the appropriate frequency

X02 %D between the original sample and the diluted result (or serial dilution) exceeded acceptance criteria

X03 Reported results not corrected for dilution factor

X04 Other (describe in comments)

Radiochemical Yield

Y01 Radiochemical tracer yield was above the upper control limit

Y02 Radiochemical tracer yield was below the lower control limit

Y03 Radiochemical tracer yield was zero

Y04 Radiochemical yield data was not present

Y05 Other (describe in comments)

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APPENDIX B

QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

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B.1. QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

This appendix provides guidance in the application of validation codes to data due to instances of multiple quality deficiencies. Quality deficiencies can be categorized based on the 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 code should not be placed on sample data until all quality deficiencies have been identified within the reporting batch.

Table B.1 provides a listing of data quality indicators and the probable effects on sample data.

Table B.1 Data Quality Indicators and Effects on Sample Data

Data Quality Indicator	Effect on Sample Data
Initial calibration	Identification and quantitation
ICV/CCV	Quantitation
Method blank	Positive bias
LCS/LCSD	Method bias and precision
MS/MSD and PDS	Positive or negative bias and precision
ICS	Positive or negative bias

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

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APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

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C.1. RULES, CALCULATIONS, AND EQUATIONS

Rounding Rules

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

Calculations/Equations

C.1 Percent Recovery (%R)

$$\%R = \frac{Measured}{Expected} x100$$

C.2 Matrix Spike (MS) Percent Recovery (%R)

$$\%R_{MS} = \frac{SSR - SR}{SA} \times 100$$

where:
SSR = Spiked sample result
SR = Sample result
SA = Spike added

C.3 Relative Percent Difference (RPD)

$$RPD = \frac{|R1 - R2|}{\overline{X}_{(R1,R2)}} \times 100$$

where:
R1 = Result
R2 = Result 2

C.4 Percent Relative Error (%RE)

$$\%RE = \frac{x' - x}{x} \times 100$$

where:
x = True value for the calibration standard
x' = Measured concentration of calibration standard

C.5 Percent Relative Standard Error (%RSE)

$$\%RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i}\right]^2 \div (n - p)}$$

where:
x_t = True value for the calibration standard
x_t' = Measured concentration of calibration standard
p = Number of terms in the fitting equation (average = 1, linear = 2, quadratic = 3)
n = Number of calibration points

C.7 Serial Dilution Percent Difference (%D)

$$\%D = \frac{\text{Initial Result - Dilution Result}}{\text{Initial Result}} \times 100$$

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