WORKING COPY

VERIF. DATE: _____

INTIALS: _____

CP2-ES-5105/FR3

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

CLEARED FOR PUBLIC RELEASE

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

Date Issued—June 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

CLEARED FOR PUBLIC RELEASE

THIS PAGE INTENTIONALLY LEFT BLANK

APPROVALS

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

CP2-ES-5105/FR3

June 2025

Approved by:

CALEB KLINE (Affiliate) **Digitally signed by CALEB KLINE (Affiliate) Date: 2025.07.07 13:45:57 -05'00'**

Caleb Kline/Date
Director, Technical Services

DOE Approval Letter: N/A Date: N/A

Effective Date: 7/9/2025

Required Review Date: 7/7/2030

Nuclear Safety Documentation: N/A per Step 6.1.1.C from CP3-NS-2001

THIS PAGE INTENTIONALLY LEFT BLANK

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	Revised text in section 5.12.5, changed limits in Table 3 and 4 in section 5.4.3, deleted text in Appendix C and nonintent changes for Bluesheet incorporation.	All	12/20/2017	Signature on file
FR2	Changed Section 5.6.5 to use professional judgment when qualifying nondetect results.	15,16	9/27/2018	Signature on file
FR2	In accordance with the Corrective Action Plan for CAPA CA-003116; Action Item AI-0004709, the periodic review date for this procedure has been extended to September 27, 2023.	All	7/6/2022	Signature on file
FR2A	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	12/13/2022	Signature on file
FR3	General revision to update plans according to DOD/DOE QSM 6.0 and other applicable professional guidance. Revision also addresses issues in CA-005356, CA-005369, and CA-005409. Revised acronyms and references, and made grammatical changes.	All	7/7/2025	Signature on file

THIS PAGE INTENTIONALLY LEFT BLANK

CONTENTS

TABLES v

ACRONYMS vii

DEFINITIONS ix

1. INTRODUCTION 1
    1.1 PURPOSE AND SCOPE 1
    1.2 APPLICABILITY 1

2. RESPONSIBILITIES 2

3. GENERAL INFORMATION 2
    3.1 LEVELS OF LABORATORY DATA DELIVERABLES 2
    3.2 STAGES OF VALIDATION 3
    3.3 DATA ASSESSMENT REVIEW 4
        3.3.1 Data Verification/Contractual Screen 4
        3.3.2 Data Validation (If Requested) 5
        3.3.3 Data Assessment 5
        3.3.4 Data Usability Assessment 5

4. DATA VERIFICATION AND VALIDATION INSTRUCTIONS 5
    4.1 SAMPLE RECEIPT CONDITIONS 6
        4.1.1 Chain-of-Custody 6
        4.1.2 Holding Time, Temperature, and Sample Preservation 6
    4.2 SAMPLE-RELATED QUALITY CONTROL RESULTS 9
        4.2.1 Blanks 9
        4.2.2 Laboratory Control Sample 12
        4.2.3 Matrix Spike/Matrix Spike Duplicate 13
        4.2.4 Duplicates 15
        4.2.5 Surrogate Standards 17
    4.3 INSTRUMENT-RELATED QUALITY CONTROL RESULTS 19
        4.3.1 Gas Chromatography/Mass Spectrometry Performance Check 19
        4.3.2 Initial Calibration 22
        4.3.3 Initial (Secondary Source) and Continuing Calibration Verification 25
        4.3.4 Internal Standards 27
    4.4 RECALCULATION CHECKS 28
        4.4.1 Reporting Limits/Sample Quantitation Limits 29
    4.5 REVIEW OF ACTUAL INSTRUMENT OUTPUTS 29
        4.5.1 Target Compound Identification 29
        4.5.2 Tentatively Identified Compounds 30

5. RECORDS 32

6. REFERENCES 33

APPENDIX A: DATA VALIDATION CODES AND DATA VALIDATION REASON CODES A-1

APPENDIX B: QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES B-1

APPENDIX C: RULES, CALCULATIONS, AND EQUATIONS C-1

TABLES

1. Responsibilities for Data Validator and SMO 2
2. Required Laboratory Report Elements 2
3. Holding Time and Sample Preservation Criteria 7
4. Holding Times and Preservation Validation Qualification Guidance 9
5. MB Validation Qualification Guidance 11
6. LCS Validation Qualification Guidance 13
7. MS/MSD Validation Qualification Guidance 15
8. Laboratory and Field Duplicate Validation Qualification Guidance 17
9. Surrogate Validation Qualification Guidance 18
10. Volatile Organic Gas Chromatography/Mass Spectrometry Tuning Criteria 19
11. Semivolatile Organic Gas Chromatography/Mass Spectrometry Tuning Criteria 19
12. Gas Chromatography/Mass Spectrometry Tuning Qualification 21
13. On-Column Standard Concentrations and Performance Criteria for Initial Calibration 22
14. Volatile and Semivolatile Target Compounds Exhibiting Poor Response 23
15. Initial Calibration Validation Qualification Guidance 25
16. ICV/CCV Performance Criteria 26
17. ICV/CCV Performance Validation Qualification Guidance 26
18. Internal Standard Validation Qualification Guidance 28

THIS PAGE INTENTIONALLY LEFT BLANK

ACRONYMS

CCV	continuing calibration verification
CFR	*Code of Federal Regulations*
COC	chain-of-custody
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DQO	data quality objective
DUP	laboratory duplicate
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
ICV	initial calibration verification
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LOD	limit of detection
LOQ	limit of quantitation
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
m/z	mass-to-charge
N/A	not applicable
PQL	practical quantitation limit
QAPP	quality assurance project plan
QC	quality control
QSM	quality systems manual
RDL	required detection limit
RF	response factor
RL	reporting limit
RPD	relative percent difference
RRF	relative response factor
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
SAEP	sampling analysis and event plan
SAP	sampling and analysis plan
SDG	sample delivery group
SMO	sample management office
SOW	statement of work
SVOA	semivolatile organic analysis
TIC	tentatively identified compound
VOA	volatile organic analysis
%D	percent difference
%R	percent recovery
%RE	percent relative error
%RSD	percent relative standard deviation
%RSE	percent relative standard error

THIS PAGE INTENTIONALLY LEFT BLANK

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

Chain-of-custody—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/mass spectrometry instrument against a traceable standard of known identity and quantity. This standardization prevails until such a time that analytical conditions are deemed out of acceptable control limits.

Internal Standard—Internal standards are nontarget compounds added to every volatile organic analysis and semivolatile organic analysis standard, blank, matrix spike, duplicate, and sample extract at a known concentration, prior to instrumental analysis. Internal standards are used as the basis for quantitation of the target compounds.

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 Level—The practical quantitation level 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 level is essentially arbitrary and not regulated by governmental agencies.

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.

Semivolatile Organic Analyte—Compounds analyzed by semivolatile analytical methods. These compounds are commonly divided into two fractions: base/neutrals and acids.

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.

Surrogate—For semivolatile organic analysis and volatile organic analysis, surrogates are nontarget standard compounds added to every blank, sample matrix spike, matrix spike duplicate, and standard used to evaluate analytical efficiency by measuring percent recovery. Semivolatile organic analysis surrogates are brominated, fluorinated, or isotopically labeled compounds that are similar to compounds of interest in chemical composition. Volatile organic analysis surrogates are brominated or deuterated compounds. Surrogates are not expected to be present in environmental media.

System Performance Check Compound—Compounds used to establish the calibration of an instrument for the SW-846 analytical methodologies applied to volatile organic analysis and semivolatile organic analysis.

Tentatively Identified Compound—Tentatively identified compounds are compounds detected in samples that are not target compounds, internal standards, system monitoring compounds, or surrogates. Up to 30 peaks (those > 10% of peak areas or heights of nearest internal standards) are subjected to mass spectral library searches for tentative identification.

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.

Volatile Organic Analysis—Method based on the purge and trap technique for organic compound analysis.

1. INTRODUCTION

1.1 PURPOSE AND SCOPE

This plan provides guidance for the verification and validation of volatile organic analysis (VOA) and semivolatile organic analysis (SVOA) 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 gas chromatography/mass spectrometry for VOA using SW-846 Method 8260 or U.S. Environmental Protection Agency (EPA) Method 624.1, and SVOA using SW-846 Method 8270, EPA Method 625.1, or other applicable gas chromatography/mass spectrometry methods (EPA 2018). 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 (i.e., SW-846 Method 8011, Appendix A of 40 *CFR* Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants*, or "Superfund Low Concentration Statement of Work" method) 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 EPA, National Functional Guidelines for Organic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

1.2 APPLICABILITY

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

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

Data validation is the process of examining a laboratory data package to provide a level of confidence in the reported analyte's identification, concentration (including detectability), and associated measurement uncertainty. The data validation process begins with a review of the laboratory data package to screen the areas of strength and weakness of the data. The data validation process continues with assessing the data against standardized procedures and criteria to confirm the presence or absence of an analyte and to evaluate

the uncertainty of the quantification for the analyte. Each data point is then qualified as to its integrity and dependability in the context of the project requirements based on all available laboratory data.

2. RESPONSIBILITIES

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

Table 1. Responsibilities for Data Validator and SMO

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

3. GENERAL INFORMATION

3.1 LEVELS OF LABORATORY DATA DELIVERABLES

Laboratory data deliverables consist of a combination of forms and raw data. Depending upon the required laboratory report elements included, the deliverable can range from Level I to an in-depth 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	✓	✓	✓	✓

Table 2. Required Laboratory Report Elements (Continued)

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
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, and equipment blanks, and field duplicates met the project requirements for frequency and field QC.

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

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

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

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

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

3.3 DATA ASSESSMENT REVIEW

The data assessment review includes the following.

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

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

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 (If Requested)

Data validation follows data verification in the data assessment review process when requested by the project team. All stages of validation 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 (U.S. Department of Energy 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.

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: Data verifier and data validator may be the same individual. The data verification/validation checklist is only completed for Stage 2B, Stage 3 and Stage 4 validations. Appendix B has qualification tables for multiple quality deficiencies.

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, 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

The data verifier shall trace custody of all samples in the reporting batch from field sampling through receipt at the laboratory by reviewing the COCs. If the information is missing, 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), indicate the problem on the data verification/validation checklist and provide this information to the data validator.

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 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, 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 VOA and SVOA 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
VOA	Water	pH ≤ 2 with hydrogen chloride, sulfuric acid, 0–6°C	14 days
	Water[a]	pH > 2 (unpreserved), 0–6°C	7 days
	Soil (EnCores)	0–6°C	48 hours[b] 14 days
	Soil, sediment, other solids	0–6°C	48 hours[b] 14 days
		SW-846-5035—low concentration pH ≤ 2 with sodium bisulfate, 0–6°C	14 days
		SW-846-5030—high concentration methanol, 0–6°C	14 days
SVOA	Water	0–6°C	7 days[c] 40 days[d]
	Soil, sediment, other solids	0–6°C	14 days[c] 40 days[d]

[a] Aqueous samples known to contain carbonates or being analyzed for select target analytes should be collected unpreserved to minimize effervescence or destruction of target analyte upon acidification. These samples are chilled to 0–6°C and have a seven-day hold time.
[b] Time from collection to preservation (freezing, pH ≤ 2, or methanol preservation).
[c] Time from collection of sample to extraction.
[d] Time from extraction to completion of analysis.

4.1.2.3 Data verification

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

the contract laboratory to determine if the omission affects sample integrity. Upon receipt, this information will be placed in the laboratory data package for delivery to the data validator. 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 noncorrectable.

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, 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 ≥ 2, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

Temperature/Preservation

Review the laboratory receiving records to determine if samples were received at the appropriate temperature and if proper preservative addition has resulted in the appropriate pH adjustment(s). **If** records demonstrate that samples were received by the laboratory at the proper temperature and with the appropriate pH adjustment, **then NO** action will be taken and no validation code will be assigned.

If temperatures are exceeded and/or pH adjustment is incorrect, **then** apply validation codes to data as follows.

- **If** samples are received without the proper pH adjustment and **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** samples are received without the proper pH adjustment and **if** the holding time is 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 are collected and analyzed for compounds with incompatible preservation (i.e., 2-chlorovinyl ether, acrolein, acrylonitrile, vinyl chloride), **then** professional judgment should be applied to determine the usability of the data.

- **If** samples are received at an elevated temperature (6°C < sample temperature ≤ 10°C), but have received the proper pH adjustment, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** samples are received at a temperature > 10°C, **then** the data validator must use professional judgment to evaluate the integrity of the reported concentrations. Data may require application of an "R" validation code.

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

- **If** samples are received with air bubbles in the vials, **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/or preservation issues.

Table 4. Holding Times and Preservation Validation Qualification Guidance

Holding Times and Sample Preservation	Validation Qualification Guidance	
Validation Step	Detects	Nondetects
1. Samples extracted and/or analyzed outside the appropriate holding time and not grossly exceeded (i.e., exceedance < 2 × holding time)	J	UJ
2. Samples extracted and/or analyzed outside grossly exceed holding time. (i.e., exceedance ≥ 2 × holding time)	J	R
3. Samples preserved improperly	J*	UJ/R*

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

4.2 SAMPLE-RELATED QUALITY CONTROL RESULTS

4.2.1 Blanks

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

Method Blank

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

Trip Blank

Trip blanks are a clean sample matrix that are taken from the bottle source (typically the laboratory) to the sampling site and then transported back to the laboratory without being exposed to sampling procedures. Trip blanks are used to assess the level of contamination that is introduced during field handling, storage,

and shipping of samples. A trip blank should be collected and included with all VOA samples collected for analysis.

Field Blank

Additionally, 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 Rinseate Blank

The equipment rinseate 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
- 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.

For VOA, the batch is an analysis batch, and the MB and samples should be analyzed within the 12-hour period beginning with the injection of 4-bromofluorobenzene.

For SVOA, the batch is a preparation batch and the MB and samples should be extracted together by the same procedure.

4.2.1.3 Criteria

Compounds that are detected in blanks analyzed must be at levels less than the method detection limit (MDL). Blank performance criteria are not specified for SW-846 methods. For the purposes of data validation, blank contamination shall be evaluated against the following guidelines found in Section 4.2.1.5.

4.2.1.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the laboratory and request that they be provided. **If** these occurrences cannot be resolved with the analytical laboratory, **then** they are considered noncorrectable problems. Apply a "B07" validation reason code to the affected data if noncorrectable deliverable deficiencies have occurred; apply only if the deviation indicates an adverse effect on data quality.

4.2.1.5 Data validation

Any compound that is reported in both the blank and the sample must be evaluated; however, if the same compound is reported in a sample and more than one blank, the sample shall be evaluated against the blank with the highest concentration of the compound. Sample results must **NOT** be modified by subtracting

blank values. When comparing blank results to analytical sample results, ensure that factors such as dilution and different sample weights have been taken into consideration.

If an MB was not analyzed with reported samples, **then** apply an "R" validation code to detected results.

If sample concentration is greater than RL and > 5 × blank concentration (10 × for common laboratory contaminants, see note below), **then** no validation code is applied.

If sample concentration is greater than RL and ≤ 5 × blank concentration (10 × for common laboratory contaminants), t**hen** apply a "J" validation code to detected results.

If sample concentration is greater than the MDL and less than or equal to the blank concentration, **then** apply a "U" validation code to detected results.

If gross contamination (saturated peaks in blank) is present, **then** apply an "R" validation code to all affected results.

NOTE: For the common laboratory contaminants such as phthalates (SVOA), methylene chloride, acetone, and 2-butanone (VOA), use a factor of 10 (i.e., 10 ×).

Table 5 summarizes data validation qualification guidance for issues with the MB.

Table 5. MB Validation Qualification Guidance

MB	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. MB **NOT** analyzed at the appropriate frequency.	R	Not applicable (N/A)
2. MB **NOT** the same matrix as the samples.	J	UJ
3. Sample result greater than RL and > 5 ×[a] blank result.	No validation code	
4. Sample result greater than RL and ≤ 5 ×[a] blank result.	J	N/A
5. Sample result less than or equal to the blank result.	U	N/A
6. Gross contamination (use professional judgment).	R	N/A
7. Instrument blank **NOT** analyzed after sample shows high concentration.	J[b]	N/A

[a] 10 × for common lab contaminants.
[b] Use professional judgment in qualifying data.

If the reviewer can determine where the contamination originated other than through blank contamination, **then** an explanation must be presented in the data validation report, and a validation code will be applied appropriately to the sample data. If large numbers of other target compounds are found at low levels in the blank, it may be indicative of a systemic laboratory problem.

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

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

4.2.2 Laboratory Control Sample

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

4.2.2.1 Deliverable

The following are deliverables.

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

4.2.2.2 Frequency

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

4.2.2.3 Criteria

The LCS **must** be analyzed and **must** fall within the DOD/DOE QSM limits.

The LCS is required for SW-846 Methods 8260 and 8270. It is recommended that this standard be the same matrix as the analytical samples, and for SVOA analysis to be prepared and analyzed with the batch of analytical samples (although the SW-846 requires analysis only). 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, extracted, and analyzed (analyzed only in the case of volatile purge and trap). All reported analytes **must** be spiked in the LCS. If an LCSD is performed, then all reported analytes **must** be spiked in the LCSD.

4.2.2.4 Data verification

Verify the presence of required reporting forms. If they are not provided, contact the laboratory and request that they be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems. Apply a “K04” validation reason code to the affected data if noncorrectable deliverable deficiencies have occurred; apply only if the deviation indicates an adverse effect on data quality.

4.2.2.5 Data validation

Confirm that the LCS was analyzed (VOA) or prepared and analyzed (SVOA). If the SVOA LCS was analyzed only (i.e., not prepared), it will provide limited value for method accuracy. The following provides guidance for the qualification of samples due to poor LCS performance. The resulting qualification of compounds is based on the number of LCS compounds outside of the laboratory determined limits and the percent recovery (%R) of those compounds.

- **If** all LCS compounds were within DOD/DOE QSM limits, **then** accept all detected and nondetected 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 target compounds. A validation code should not be applied to nondetected target compounds.

- **If** the LCS %R for an analyte is less than the DOD/DOE QSM lower acceptance limit, **then** apply a "J" validation code to detected target compounds and apply an "R" validation code to nondetected result (use professional judgment).

- **If** an LCSD is included with the analyses and the calculated %RPD between the LCS and LCSD results exceeds 30%, **then** apply a "J" validation code to associated detections. A validation code should not be applied to nondetected target compounds.

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

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

Table 6. LCS Validation Qualification Guidance

LCS	**Validation Qualification Guidance**	
Validation Step	Detects	Nondetects
1. LCS **NOT** analyzed at the proper frequency.	J	UJ
2. LCS **NOT** prepared and analyzed.	R	R
3. %R greater than DOD/DOE QSM upper acceptance limit or RPD > 30%.	J	**No validation code**
4. %R < DOD/DOE QSM lower acceptance limit.	J	R
5. Analyte not spiked in LCS/LCSD.	R	R

4.2.3 Matrix Spike/Matrix Spike Duplicate

The purpose of the MS/MSD in SW-846 Method 8260 and Method 8270 is to determine whether the sample matrix contributes bias to the analytical results. **If the MS/MSD** recovery 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/LCSD also are analyzed to verify method accuracy. **If** only the MS/MSD are affected, **then** a matrix effect is likely.

4.2.3.1 Deliverables

The following are deliverables.

- 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.

4.2.3.3 Criteria

For SW-846 methods, the MS/MSD %R should fall within DOD/DOE QSM limits. If MS/MSD results fall outside the laboratory-determined limits, 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).

4.2.3.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the laboratory and request that they be provided. **If** these occurrences cannot be resolved with the analytical laboratory, **then** they are considered noncorrectable problems. Apply an "M05" validation reason code to the affected data **if** noncorrectable deliverable deficiencies have occurred; **then** apply only if the deviation indicates an adverse effect on data quality.

4.2.3.5 Data validation

A determination shall be made concerning what extent that noncompliant MS/MSD recoveries have on other sample data regarding the MS/MSD sample itself, as well as specific compounds in samples associated with the MS/MSD. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, then 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. The MS/MSD also shall be reviewed to determine **if** there is an overall bias to the sample or base neutral acid fraction, such as the majority of compounds with either a high or low recovery. MS/MSD recoveries alone shall not be used exclusively for application of validation codes, but in conjunction with other supporting QC data. Professional judgment shall be used to determine the need for applying validation codes to reported compounds.

If MS/MSD analysis was required, but not performed, **then** apply a validation code 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 precision in the measurable range of the method.

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

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

If the MS or MSD has been provided and recovery difficulties have been noted, 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.

- **If** poor spike recovery occurs in a sample whose concentration is > 4 × the spiked amount. Professional and technical judgment should be used in whether application of a validation code to data is warranted.

- **If** MS %R > upper control limit, **then** apply a "J" validation code to detected results and do not apply a validation code to nondetected results.

- **If** MS %R > 10% and < lower control limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

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

If a poor duplicate or MS/MSD precision is observed, the following guidance shall be used.

- **If** the RPD for MS/MSD is > 30%, **then** apply a "J" validation code to associated detected results. A validation code is not required on nondetected results.

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

Table 7. MS/MSD Validation Qualification Guidance

MS/MSD	Validation Qualification Guidance	
Validation Step	Detects	Nondetects
1. MS/MSD **NOT** analyzed at the appropriate frequency.	J	UJ
2. %R greater than upper acceptance limit or RPD > 30%.	J	No validation code
3. 10% < %R < lower acceptance limit.	J	UJ
4. %R < 10%.	J	R
5. Analyte **NOT** spiked in MS/MSD.	R	R

NOTE: For an MS that does not meet the acceptance criteria, apply validation codes to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, 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 reviewer also should use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the laboratory data package. The reviewer 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 reviewer may determine that no samples are sufficiently similar to the sample used for the MS and, thus, that only the field sample used to prepare the MS sample should be qualified.

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 homogenous and most soil/sediment samples are homogenous within a factor of two or three.

4.2.4.1 Deliverables

The following are deliverables.

- 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.

- Samples identified as field blanks must not be analyzed as laboratory duplicates.
- For sample concentrations > 5 × RL, the laboratory duplicate precision for aqueous samples as measured by RPD must be within ± 25% for both VOA and SVOA analyses (lab duplicates and field duplicates). For solid matrices, the RPD must be within ± 40% (lab and field duplicates) for both VOA and SVOA analyses. If the sample results are < 5 × RL, RPD does not apply. Instead, the absolute difference between the sample and duplicate must be < 5 × RL.

4.2.4.4 Data verification

The data verifier shall verify that field blanks were not analyzed as laboratory duplicates. **If** a field blank has been used, **then** the SMO will be notified immediately to ensure timely corrective action. **If** reanalysis cannot be completed, **then** this issue will be identified as noncorrectable on the data verification/validation checklist.

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

If the missing information cannot be obtained from the laboratory, **then** it is considered as noncorrectable problems and shall be identified in this way on the data verification/validation checklist. As they are contract compliance related, all such occurrences shall be communicated to SMO and to the data validator on the data verification/validation checklist.

4.2.4.5 Data validation

The following are data validation steps.

- 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.

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	Qualification Instructions
Laboratory Duplicate	Aqueous	> 25%	Sample and DUP ≥ 5 × RL	Results greater than RL "J" Nondetect results "UJ"
	Solid	> 40%		
	Aqueous	N/A	Sample and DUP < 5 × RL	Absolute difference greater than RL "J" Absolute difference less than RL **NO** action
Laboratory Duplicate (continued)	Solid	N/A	Sample and DUP < 5 × RL	Absolute difference greater than RL "J" Absolute difference less than RL **NO** action
Field Duplicate	Aqueous	> 25%	Sample and DUP ≥ 5 × RL	Results greater than RL "J" Nondetect results "UJ"
	Solid	> 40%		
	Aqueous	N/A	Sample and DUP < 5 × RL	Absolute difference greater than RL "J" Absolute difference less than RL **NO** action
	Solid	N/A		

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., 35% RPD, 5 × 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 Surrogate Standards

Surrogate standards are nontarget compounds added to all analytical samples, blanks, and QC samples to assess the overall system performance. For volatile analysis, surrogate standards are added to water matrices prior to gas chromatography/mass spectrometry purge and for soil matrices before extraction. For semivolatiles, surrogate standards are added prior to the extraction for water and soil matrices.

4.2.5.1 Deliverables

The following are deliverables.

- Surrogate recovery reports for all samples, blanks, and QC samples
- Raw data (required for confirmation)

4.2.5.2 Frequency

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

4.2.5.3 Performance criteria

The surrogate recoveries are evaluated against the laboratory determined limits.

4.2.5.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the laboratory and request that they be provided. **If** these occurrences cannot be resolved with the analytical laboratory, **then** they are considered noncorrectable problems. Apply an "S06" validation reason code to the affected data **if** noncorrectable deliverable deficiencies have occurred; **then** apply only if the deviation indicates an adverse effect on data quality.

4.2.5.5 Data validation

Apply a validation code if either of the following conditions are met:

- One or more volatile surrogates is out of criteria, or

- One or more base-neutrals or one or more acid surrogates are out of criteria for semivolatiles. Professional judgment must be used if recovery is suspected to be affected by matrix interferences.

Volatile Analysis

- **If** any surrogate %R exceeds the upper control limit, **then** apply a "J" validation code to detected results and apply no validation code to nondetected results.

- **If** any surrogate %R is between 10% and the lower control limit, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

- **If** any surrogate %R < 10%, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

- **If** surrogates are "diluted out," **then** the data validator must use professional judgment to determine if application of a validation code to data is necessary.

Semivolatile Analysis

- **If** the surrogate %R exceeds the upper acceptance limit, **then** apply a "J" validation code to detected results for that fraction and apply no validation code to nondetected results.

- **If** one or more base-neutral or acid surrogate %R is between 10% and the lower control limit, **then** apply a "J" validation code to detected results for that fraction and apply a "UJ" validation code to nondetected results for that fraction.

- **If** any surrogate %R < 10%, **then** apply a "J" validation code to detected results for that fraction and apply an "R" validation code to nondetected results for that fraction.

- **If** surrogates are "diluted out," **then** the data validator must use professional judgment to determine if application of validation codes to the data is necessary.

- **If** recalculation of the surrogate concentrations or recoveries do not agree within 10%, **then** professional judgment should be used to determine impact on the reported data.

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

Table 9. Surrogate Validation Qualification Guidance

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

*Apply validation code only if the deviation indicates an adverse effect on data quality.

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

- Surrogate percent recoveries
- Holding times
- Comparison of concentration of target compounds
- Internal standard areas and retention time

4.3 INSTRUMENT-RELATED QUALITY CONTROL RESULTS

4.3.1 Gas Chromatography/Mass Spectrometry Performance Check

4.3.1.1 Deliverables

The following are deliverables.

- Instrument performance check summary for each gas chromatography/mass spectrometry system used
- Raw data (required for confirmation)

4.3.1.2 Frequency

The instrument performance check must be analyzed at the beginning of each 12-hour period during which samples and/or standards are analyzed. **If** samples are analyzed for volatiles by EPA Method 8260D and semivolatiles by EPA Method 8270E, **then** an instrument performance check is only required prior to the initial calibration, and a mid-point CCV standard must be analyzed once every 12-hour period, prior to sample analysis and at the end of sample analysis.

4.3.1.3 Criteria

Table 10 and Table 11 present ion abundance criteria for SW-846 Methods 8260D and 8270E, respectively. Alternate tuning criteria may be employed (e.g., EPA Method 625) provided that method performance is not adversely affected.

Table 10. Volatile Organic Gas Chromatography/Mass Spectrometry Tuning Criteria

Mass-to-Charge (m/z)	Ion Abundance Criteria (SW-846 Method 8260D)*
95	Base peak, 100% relative abundance 50–200% of m/z174
96	5.0–9.0% of m/z 95 (5.0–15.0% when using hydrogen carrier)
173	< 2.0% of m/z 174
174	50.0–200% of m/z 95
175	5.0–9.0% of m/z 174
176	> 95.0%, but < 105.0% of m/z 174
177	5.0–10.0% of m/z 176

*All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 200% that of m/z 95.

Table 11. Semivolatile Organic Gas Chromatography/Mass Spectrometry Tuning Criteria

m/z	Ion Abundance Criteria (SW–846 Method 8270E)
68	< 2.0% of m/z 69
69	Present

Table 11. Semivolatile Organic Gas Chromatography/Mass Spectrometry Tuning Criteria (Continued)

m/z	Ion Abundance Criteria (SW–846 Method 8270E)
70	< 2.0 of m/z 69
197	< 2.0% of m/z 198
198	Base peak or present
199	5.0–9.0% of m/z 198
365	> 1.0% of m/z 198
441	< 150% of m/z 443
442	Base peak or present
443	15.0–24.0% of m/z 442

NOTE: All ion abundances for SVOA analysis should be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may exceed that of m/z 198.

NOTE: For EPA Method 8270, a performance check should be performed using a solution containing 4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT), benzidine, and pentachlorophenol. The degradation of 4,4'-DDT to 4,4'-dichlorodiphenyldichloroethylene and 4,4'-dichlorodiphenyldichloroethane should be ≤ 20%. Benzidine and pentachlorophenol should be present at their normal responses and should not exceed a tailing factor of 2. A performance check is not required when analyzing only for polycyclic aromatic hydrocarbons or polychlorinated biphenyls.

4.3.1.4 Data verification

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

4.3.1.5 Data validation

The data validator shall review the data verification/validation checklist to confirm the presence of the instrument performance check summary for VOA and SVOA analyses. **If** the data verification/validation checklist notes that the instrument performance check summary is missing and these occurrences cannot be resolved with the contract laboratory, **then** they are considered noncorrectable problems. Apply a "P05" validation reason code to the affected data **if** noncorrectable deliverable deficiencies have occurred; apply validation codes only **if** the deviation indicates an adverse effect on data quality.

If mass assignment is in error (such as m/z 199 is indicated as the base peak for SVOA analysis, rather than m/z 198), **then** apply an "R" validation code to all results

The following ion abundances **must** be satisfied.

- VOA ion abundances: m/z 95/96, 174/175, 174/176, 176/177
- SVOA ion abundances: m/z 198/199, 442/443, 68, 70, 197, 441

Raw data should be consulted to determine if associated sample and QC data can be considered usable or unusable if the criteria for critical or noncritical ion-abundances are not met. Guidance to aid the application of the evaluation of semivolatile compounds is as follows:

- M/z 198/199 and 442/443 are based on the natural abundances of C-12 and C-13 and should always be met.

- M/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of resolution adjustment.

- M/z 365 is an indicator of suitable instrument zero adjustment. If m/z 365 is zero, minimum detection limits may be affected. If m/z 365 is present, but < 0.75%, the deficiency is not as serious.

- For Stage 3 and Stage 4 data validation only, conduct raw data confirmation of one of the ion abundance summaries. Inspect raw data to ensure that during the instrument performance check, three scans (apex and scans immediately preceding and following the apex) have been averaged and that a scan no more than 20 scans preceding the elution of 4-bromofluorobenzene or decafluorotriphenylphosphine is used for background subtraction.

- **If** it is found that the laboratory made only minor calculation errors that do not affect the data quality, **NO** application of validation codes to the data is required.

If m/z ratios are not within the ion abundance criteria given within Tables 10 and 11, using the criteria indicated in the preceding paragraphs and using validation reason code "P06," **then** the data validator should use professional judgment in deciding the impact of the reported instrument performance of the data.

If the degradation of 4,4'-DDT is > 20% and ≤ 40%, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

If the degradation of 4,4'-DDT is > 40%, **then** apply an "R" validation code to detected and nondetected results.

If the tailing factor is > 2 and ≤ 4, **then** apply a "J" validation code to detected results and a "UJ" validation code to nondetected results.

If the tailing factor is > 4, **then** apply an "R" validation code to the detected and nondetected results.

Table 12 summarizes data validation qualification guidance for issues with GC/MS tuning.

Table 12. Gas Chromatography/Mass Spectrometry Tuning Qualification

Gas Chromatography/Mass Spectrometry Performance Check	Validation Qualification Guidance	
Validation Step	Detects	Nondetects
1. Gas Chromatography/Mass Spectrometry instrument performance check not performed at the proper frequency.	R*	R*
2. Incorrect mass ion assignment.	R	R
3. Degradation of 4,4'-DDT > 20% and ≤ 40%.	J	UJ
4. Degradation of 4,4'-DDT > 40%.	R	R
5. Tailing factor > 2 and ≤ 4.	J	UJ
6. Tailing factor > 4.	R	R
7. Instrument performance did not meet abundance criteria.	Refer to Table 9 in Section 4.2 and Table 10 in Section 4.3 or the method being reviewed	
8. The proper averaging of scans reported in raw data (Stage 4 validation only).	Refer to Section 4.3 or the method being reviewed	

*Apply a validation code only if the deviation indicates an adverse effect on data quality.

4.3.2 Initial Calibration

Compliance requirements for satisfactory instrument calibration ensure that the instrument is capable of producing acceptable qualitative and quantitative data for volatile and semivolatile compounds on the target compound list. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run and of producing a linear calibration curve.

4.3.2.1 Deliverables

The following are deliverables.

- Initial calibration summary for SW-846 methods
- Raw data (required for confirmation)

4.3.2.2 Frequency

Initial calibration must be performed within 12 hours of the instrument performance check and prior to sample analysis.

4.3.2.3 Criteria

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

Table 13 summarizes the on-column standard concentrations and performance criteria for initial calibration.

Table 13. On-Column Standard Concentrations and Performance Criteria for Initial Calibration

SW-486 Method 8260 (VOA) Method 8270 (SVOA)
Lowest concentration at the RL
Five levels minimum for average response factor (RF)/calibration factor, lowest concentration at or below the RL
Six levels minimum for quadratic model
Seven levels minimum for cubic model
Average response calibration: RSD ≤ 20.0%
Linear calibration option: $r^2 \geq 0.99$
Quadratic calibration option: $r^2 \geq 0.99$

4.3.2.4 Data verification

The data verifier shall confirm the presence of required reporting forms. If they are not provided, contact the laboratory and request that they be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification/validation checklist. Apply a “C07” validation reason code to affected data, if noncorrectable

deliverable deficiencies have occurred. Apply validation codes only if the deviation indicates an adverse effect on data quality.

4.3.2.5 Data validation

Due to reduced instrument sensitivity, validation codes are applied to all samples related to the initial calibration **if** the initial relative response factor (RRF) of any compound is < 0.05 or 0.01 (for compounds listed in Table 14). Because results at or near the instrument detection limit are impacted, an "R" validation code is applied to nondetected results due to the potential for reporting false negatives. A "J" validation code is applied to detected results.

Table 14. Volatile and Semivolatile Target Compounds Exhibiting Poor Response

Volatile Compounds		Semivolatile Compounds	
Acetone	Isopropylbenzene	2,2'-Oxybis-(1-chloropropane)	Benzaldehyde
2-Butanone	Methyl acetate	4-Chloroaniline	4-Nitroaniline
Carbon disulfide	Methylene chloride	Hexachlorobutadiene	4,6-Dinitro-2-methylphenol
Chloroethane	Methylcyclohexane	2,3,4,6-Tetrachlorophenol	N-Nitrosodiphenylamine
Cyclohexane	Methyl tert-butyl ether	2-Nitroaniline	3,3'-Dichlorobenzidine
1,2-Dibromethane	*trans*-1,2-Dichloroethene	3-Nitroaniline	1,1'-Biphenyl
Dichlorodifluoromethane	4-Methyl-2-pentanone	2,4-Dinitrophenol	Dimethylphthalate
cis-1,2-Dichloroethene	2-Hexanone	4-Nitrophenol	Diethylphthalate
1,2-Dichloropropane	Trichlorofluoromethane	Acetophenone	1,2,4,5-Tetrachlorobenzene
1,2-Dibromo-3-chloropropane	1,1,2-Trichloro-1,2,2-trifluoroethane	Caprolactam	Carbazole
1,4-Dioxane	-	Atrazine	Butylbenzylphthalate
-	-	Di-n-butylphthalate	Di-n-octylphthalate
-	-	Bis(2-ethylhexyl)phthalate	-

If the percent relative standard deviation (%RSD) exceeds ± 20% for a target analyte, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results, unless a linear or higher order calibration curve was performed.

Nonlinearity in the calibration curve is indicated **if** the %RSD is > 20%. The laboratory may elect to calculate a linear or quadratic calibration curve. **If** this method is used, there are two options as follows: **Option 1**: linear least squares regression $r^2 \geq 0.9905$; or **Option 2**: nonlinear regression coefficient of determination $r^2 \geq 0.99$ (6 points shall be used for second order). A value of zero should not be included as a calibration point. Although forcing the regression through the origin is allowable, results should not be reported below the calibration range. Calibration curves that are higher than second order are not allowed in accordance with DOD/DOE QSM requirements. **If** a linear or quadratic calibration curve is used, **then** the percent relative error (%RE) or percent relative standard error (%RSE) must be evaluated at or near the mid-range of the initial calibration and at less than or equal to the RL. The maximum allowable %RE at or near the mid-range and low level of the calibration shall be 20% and 50%, respectively. The maximum allowable %RSE shall be 30%.

If $0.90 < r^2 < 0.99$, **then** apply a "J" validation code to the detected result and apply a "UJ" validation code to the nondetected result.

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

If %RE > 20% or 50% at or near the mid-range and low level of the calibration, respectively, **then** apply a "J" validation code to the detected results and apply a "UJ" validation code to the nondetected results.

If %RSE > 30%, **then** apply a "J" validation code to the detected results and apply a "UJ" validation code to the nondetected results.

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

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

If the target analytes were not calibrated, **then** apply an "R" validation code to the detected and nondetected results.

If less than the required minimum number of calibration standards, **then** apply an "R" validation code to the detected and nondetected results.

If the laboratory did not use all of the analyzed calibration standards in the target analyte curve, **then** apply an "R" validation code to the detected and nondetected results.

If the lowest calibration standard is higher than the RL, **then** apply a "J" validation code to the detected results and apply a "UJ" validation codes to the nondetected results.

For Stage 4 data validation only, conduct raw data confirmation by inspecting for instances of manual integrations of peak areas. Recurring manual integrations on similar peaks within a calibration, manual integrations on peaks with normally good symmetry, and peak splitting manual integrations shall be inspected to determine the necessity for integration or if a systematic problem is occurring in the analyses.

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

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

Raw data must be consulted before applying validation codes based on initial calibration alone. Checks must be made for saturation, baseline shift, peak splitting, and other obvious interferences.

Table 15 summarizes data validation qualification guidance for the initial calibration.

Table 15. Initial Calibration Validation Qualification Guidance

Initial Calibration	Validation Qualification Guidance	
Validation Step	Detects	Nondetects
1. Initial Calibration **NOT** performed	R	R
2. The compounds' average RRF < 0.05 or < 0.01*.	J	R
3. %RSD of calibration points > 20%*.	J	UJ
4. Do samples with differing matrices have matching initial calibration matrices?	Refer to Section 4.3.2.5 or the method being reviewed	
5. Sample concentration exceeds calibration range.	J	N/A
6. $0.90 < r^2 < 0.99$	J	UJ
7. $r^2 < 0.90$	J	R
8. %RE > 20% or 50% at or near the mid-range and low level of the calibration, respectively.	J	UJ
9. %RSE > 30%	J	UJ
10. Less than the required minimum calibration standards analyzed.	R	R
11. All analyzed calibration standards are not used in the calibration.	R	R
12. Lowest calibration standard greater than RL.	J	UJ
13. Have raw data been examined for anomalies? (Stage 4 validation only).	Refer to Section 4.3.2.5 or the method being reviewed	
14. Have the quantitation ions of two compounds been confirmed at the correct ions for quantitation? (Stage 4 validation only).	Refer to Section 4.3.2.5 or the method being reviewed	
15. Have raw data been inspected for manual integrations? (Stage 4 validation only).	Refer to Section 4.3.2.5 or the method being reviewed	

*Poor response compounds (Table 14).

4.3.3 Initial (Secondary Source) and Continuing Calibration Verification

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

4.3.3.1 Deliverables

The following are deliverables.

- Continuing calibration (ICV/CCV) summary for each gas chromatography/mass spectrometry system used
- Raw data (required for confirmation)

4.3.3.2 Frequency

Calibration is verified for VOA and SVOA initially following calibration and once per 12-hour period in which samples are analyzed. The continuing calibration standard must be analyzed prior to and at the end of sample analysis.

4.3.3.3 Criteria

Table 16 lists performance criteria for ICV/CCV.

Table 16. ICV/CCV Performance Criteria

SW-846 Method 8260 (VOA) Method 8270 (SVOA)
• Mid-level standard—run every 12 hours
• 8260 and 8270—percent difference (%D) ≤ 20% for opening CCV • 8260 and 8270—%D ≤ 50% for closing CCV

4.3.3.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the laboratory and request that they be provided. **If** these occurrences cannot be resolved with the analytical laboratory, **then** they are considered noncorrectable problems and **shall** be identified in this way in the data validation report. Apply a "C07" validation reason code to the affected data if noncorrectable deliverable deficiencies have occurred; apply only if the deviation indicates an adverse effect on data quality.

4.3.3.5 Data validation

If the %D exceeds ± 20% for ICV analyses, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

If the %D exceeds ± 20% for opening CCV or ± 50% for closing CCV, **then** apply a "J" validation code to detected results and apply a "UJ" to nondetected results.

If the %D exceeds ± 50% for ICV or opening CCV or ± 80% for closing CCV, **then** apply an "R" validation code to detected and nondetected results.

If the RRF is < 0.05 or < 0.01 for compounds in Table 14, **then** apply a "J" validation code to detected results with acceptable mass spectral identification and use professional judgment when applying nondetected results.

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, **then** apply an "R" validation code to detected and nondetected results.

For Stage 3 and Stage 4 validation only, conduct raw data confirmation by confirming the quantitation ions of two compounds in the continuing calibration to determine whether the correct quantitation ions have been used to quantify the compounds. **If** incorrect ions have been shown, **then** rationale should be provided in the data package for the noncompliance.

Table 17 summarizes data validation qualification guidance for issues with the ICV/CCV.

Table 17. ICV/CCV Performance Validation Qualification Guidance

Continuing Calibration	Validation Qualification Guidance	
Validation Step	Detects	Nondetects
1. CCV **NOT** analyzed prior to or at the end of sample analysis or every 12 hours.	R	R
2. ICV **NOT** analyzed after initial calibration and prior to sample analysis.	R	R
3. The %D for ICV or opening CCV > 20% ≤ 50%.	J	UJ
4. The %D for ICV or opening CCV > 50%.	R	R
5. The %D for closing CCV > 50% ≤ 80%.	J	UJ
6. The %D for closing CCV > 80%.	R	R
7. RRF < 0.05 or < 0.01 for compounds in Table 14 and %D > 20%.	J	*

*Use professional judgment when applying validation codes to nondetected results.

4.3.4 Internal Standards

Internal standards are used to ensure that gas chromatography/mass spectrometry sensitivity and response are stable during analysis.

4.3.4.1 Deliverables

The following are deliverables.

- Internal standard area and RT summary
- Raw data (required for confirmation)

4.3.4.2 Frequency

Internal standards are added to all analytical samples, blanks, and QC samples prior to purging for volatile water and soils and are added after extraction and prior to analysis of semivolatile water and soil extractions.

4.3.4.3 Criteria

The retention time of the internal standard compound in the sample or blank must not vary more than ± 10.0 seconds from the RT of the same internal standard in the associated opening CCV or mid-point standard from the associated initial calibration. The area response of each internal standard compound in all samples and blanks must be within the inclusive range of 50–200% of the area response of the same internal standard from the associated opening CCV or the mid-point standard from the associated initial calibration.

4.3.4.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO and request that they be provided. **If** these occurrences cannot be resolved with the analytical laboratory, **then** they are considered noncorrectable problems. Apply an "I07" validation reason code to affected data if noncorrectable deliverable deficiencies have occurred; apply only if the deviation indicates an adverse effect on data quality.

4.3.4.5 Data validation

The following provides guidance for applying validation codes to samples due to poor internal standard performance. Application of validation codes to compound results is based on the associated internal standard.

If peak area %D < 50%, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results.

If peak area %D > 200%, **then** apply a "J" validation code to detected results and apply no validation code to nondetected results.

If a performance drop is indicated by extremely low area counts (< 20%), **then** apply an "R" validation code to detected and nondetected results.

If internal standard retention times vary by more than ± 10 seconds (between the sample internal standard and calibration internal standard), conduct confirmation of raw data for Stage 4 data validation only by examining the chromatographic profile for that sample to determine if any false positives or negatives exist; **then** use professional judgment when appropriate to apply validation code to false positive results or false negative detection limits.

Table 18 summarizes data validation qualification guidance for issues with the internal standards.

Table 18. Internal Standard Validation Qualification Guidance

Internal Standards	Validation Qualification Guidance	
Validation Step	Detects	Nondetects
1. Proper internal standards **NOT** used.	R[a]	R[a]
2. Samples, blanks, and QC samples **NOT** fortified with internal standards.	R[a]	R[a]
3. %D < 20%	R	R
4. %D < 50%	J	UJ
5. %D > 200%	J	N/A
6. Extremely low area counts in more than one area.	J/R	R
7. Internal standard retention time ± 10 seconds from continuing calibration.	J/R[b]	R[b]

[a] Apply validation code only if the deviation indicates an adverse effect on data quality.
[b] Apply validation code as appropriate.

4.4 RECALCULATION CHECKS

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

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

4.4.1 Reporting Limits/Sample Quantitation Limits

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

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.

4.4.1.1 Deliverables

The following is a deliverable.

- Sample Summary/Sample Data Sheets

4.4.1.2 Frequency

RLs are reported for all compounds that are not detected above the method MDL.

4.4.1.3 Data verification

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

4.4.1.4 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.

Calculations for modifications to the RL can be found in Appendix C.

4.5 REVIEW OF ACTUAL INSTRUMENT OUTPUTS

4.5.1 Target Compound Identification

4.5.1.1 Deliverables

The following are deliverables.

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

4.5.1.2 Criteria

Mass spectra of the sample target compound and a current laboratory-generated standard must match according to the following criteria. All ions present in the standard mass spectrum at a relative intensity > 10% must be present in the sample spectrum.

All ions > 10% relative intensity in the standard reference spectrum must be present in the sample mass spectrum. All ions > 10% relative intensity in the sample mass spectrum, but not present in the standard mass spectrum, must be considered and accounted for.

The relative intensities of the ions must agree within ± 20% between the standard and sample spectrum.

The relative retention time (RRT) of the target compound must be within ± 0.06 units of the standard RRT.

4.5.1.3 Data validation

The presence and/or absence and concentration of detected compounds in the samples are reviewed to determine whether the correct quantitation ions have been used for proper quantification of the compounds. **If** incorrect ions have been shown, **then** rationale should be provided in the data package for the noncompliance. **If** no rationale has been provided, **then** evaluation of the effect on the quantitation of detected target compounds shall be made. **If** detected target compounds quantified against the incorrect ion are significantly affected, **then** apply an "R" validation code to the affected compounds.

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

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

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

4.5.2 Tentatively Identified Compounds

Tentatively identified compounds (TICs) are nontarget compounds that are not system-monitoring compounds or internal standards. TICs are not always reported by the laboratory. If TICs are required for a project, then the requirement to report them will be included in the laboratory SOW.

4.5.2.1 Deliverables

The following are deliverables.

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

4.5.2.2 Criteria

TICs are qualitatively identified by using mass spectral identification from a mass spectra library search. The laboratory must identify the 10 largest VOA peaks and 20 SVOA peaks that are not surrogates, internal standards, or target compounds.

4.5.2.3 Data verification

Verify the presence of the required reporting forms. If the required reporting forms are not present and these occurrences are considered noncorrectable problems, indicate this on the data verification/validation checklist.

4.5.2.4 Data validation

Check raw data against the TIC report to ensure that all TIC peaks are accounted on sample summary sample data sheets.

Two named TIC concentrations (not "unknowns") **shall** be recalculated using the calculations in Appendix C with a RRF of 1.0.

The following are guidance for identification/and application of validation codes to TICs:

- Apply "NJ" to all TICs presumptively identified, at estimated concentration.
- Mass spectra for all samples with raw data and blanks shall be examined for TICs.
- All ions > 10% relative intensity in the reference spectrum should be in the sample spectrum.
- Relative intensity of the major ions should agree within $\pm$ 20% between sample and reference spectra.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination, interference, or co-elution of additional TIC or target compounds.
- **If** the identification is uncertain or there are extenuating factors affecting compound identification, **then** the TIC result may be reported as "unknown."
- TICs < 10× the level in the blank should not be reported. **If** a TIC is reported at this level, **then** apply an "R" validation code.
- TICs may be reported as "either compound X or compound Y" **if** there are more than one reasonable match from the library search.
- All similar TICs may be reported as a total (e.g., all alkanes may be reported as total hydrocarbons).
- **If** TIC evaluation from a library search does not yield conclusive evidence from items stated above, change the identification of the TIC to "unknown"; **then** professional judgment shall be used in comparing references spectra to sample spectra and the incidence of TICs in multiple samples and blanks.
- Common laboratory artifacts should not be reported as TICs. Apply an "R" validation code to these compounds **if** reported as TICs.
- **If** a TIC is reported in one or all samples but not in the blank, **then** check if the compound is a common laboratory artifact in the sample and inspect the blank for peaks that are < 10% of the internal standard

area, but are present in the blank chromatogram at a similar retention time. Apply an "R" validation code to compounds.

- An "R" validation code shall be applied to compounds reported as a TIC in one fraction **if** that compound is reported as detected in another fraction.

- Blank chromatograms shall be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level nontarget compound, which is a common artifact or laboratory contaminant, is detected in a sample, a thorough check of blank chromatograms may require looking for peaks that are < 10% of the internal standard area but present in the blank's chromatogram at similar relative retention time.

- **If** target compounds are identified by nontarget library searches, **then** the laboratory shall be contacted to resubmit the relevant forms with the target compound quantified against the correct quantitation ion.

The following list presents the common laboratory contaminants that should not be reported as TICs in either VOA or SVOA fractions.

Common Laboratory Contaminants

- Carbon dioxide (m/z 44), (may be introduced by system leaks)
- Siloxanes (m/z 73) (common gas chromatography column bleed artifacts)
- Diethyl ether (1,1-oxybisethane)
- Hexane
- 1,1,2-trichloro-1,2,2-trifluoroethane (flurotrichloromethane or Freon 113)
- Phthalates at levels < 100 µg/L (waters) or 4,000 µg/Kg (soils)

Solvent Preservatives and By-Products

- Cyclohexane
- Cyclohexanone
- Cyclohexenone
- Cyclohexanol
- Chlorocyclohexene
- Chlorocyclohexanol

Aldol Reaction Products of Acetone

- 4-methyl-2-penten-2-one
- 4-hydroxy-4-methyl-2-pentanone
- 5,5-dimethyl-2(5H)-furanone

5. RECORDS

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

- Data verification/validation checklist (Stage 2B, Stage 3, and Stage 4 validation)
- Data validation report (Stage 2B, Stage 3, and Stage 4 validation)
- Copies of qualified or unqualified results reports (if applicable)

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*

EPA 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.

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

THIS PAGE INTENTIONALLY LEFT BLANK

APPENDIX A

DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

THIS PAGE INTENTIONALLY LEFT BLANK

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

Data Validation Codes

U Analyte compound or nuclide considered not detected above the reported detection limit.

J Analyte compound or nuclide identified; the associated numerical value is approximated.

NJ Analyte compound or nuclide presumptively present at an estimated quantity.

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 is not usable for its intended purpose.

= "Equals" sign, indicates that no qualifier is necessary.

Data Validation Reason Codes

Blanks

B01 Sample concentration was less than the reporting limit (RL), and ≤ 5 × the blank concentration (10 × for common contaminants).

B02 Sample concentration was greater than the RL, and ≤ 5 × the blank concentration (10 × for common contaminants).

B03 Gross contamination exists; blank result impacted associated analyte data quality.

B04 Negative blank result impacted associated analyte data quality.

B05 Blanks were not analyzed at appropriate frequency.

B06 Sample not significantly different than radiochemical method blank.

B07 Blank data not reported.

B08 Instrument blank not analyzed after high-level sample.

B09 Other (describe in comments)

B10 Method blanks not extracted at appropriate frequency.

B11 Sample results were corrected for blank contamination.

B12 Blank was not the same matrix as the analytical samples.

B13 Concentration of target compound detected in sample affected by carryover.

Calibration

C01 Initial calibration average relative response factor (RRF) was < 0.05 or < 0.01 for compounds in Table 14
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 compounds in Table 14
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
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

Calibration

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 was exhibited by a major drop-off
I04 Internal standard retention time varied by more than 30 seconds
I05 Inappropriate internal standard used
I06 Inappropriate internal standard concentration(s) used

Internal Standards

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 MS/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
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

Quantitation

Q21 Isotopes of same radionuclide do not show equilibrium
Q22 Peak not within appropriate energy range
Q23 Counting uncertainty ≥ 80% of sample result
Q24 Raw data anomaly
Q25 Other (describe in comments)
Q26 Retention Time (RT) outside calculated RT window
Q28 Neither RL or the sample quantitation limit (SQL) are reported for a nondetect result
Q29 SQL greater than RL
Q30 Compound detected at less than SQL and not qualified “J”
Q31 Presence of high molecular weight contaminants impacted sample quantitation

Surrogates

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

Instrument Tuning

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

Pesticide Sample Cleanup

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

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)

THIS PAGE INTENTIONALLY LEFT BLANK

APPENDIX B

QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

THIS PAGE INTENTIONALLY LEFT BLANK

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.

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

Data Quality Indicator	Effect on Sample Data
Gas chromatography/mass spectrometry tuning	Compound identification
Initial calibration	Identification and quantitation
Continuing calibration	Quantitation
Surrogate standards	Positive or negative bias
Internal standards	Positive or negative bias
Method blank	Positive bias
Laboratory control sample (LCS)/LCS duplicate	Method bias and precision
Matrix spike (MS)/MS duplicate	Positive or negative bias and precision
Quality control check standard	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.

THIS PAGE INTENTIONALLY LEFT BLANK

APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

THIS PAGE INTENTIONALLY LEFT BLANK

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 Calculation for Relative Response Factor (RRF)

$$RRF = \frac{A_x}{A_{is}} x \frac{C_{is}}{C_x}$$

where:
- A_x = Area of the characteristic ion of the compound
- A_{is} = Area of the characteristic ion of the internal standard
- C_x = Concentration of the compound
- C_{is} = Concentration of the internal standard

C.2 Calculation for Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{\sigma}{\overline{X}_{(R1,R2)}} x100$$

where:
- σ = Standard deviation of the five initial calibration RRFs (per compound)
- $X_{(R1,R2)}$ = Mean of the five initial calibration RRFs (per compound)

C.3 Surrogate Standard Concentration

$$C_{ss} = \frac{A_{ss} x I_s}{A_{is} x RRF_{50}}$$

where:
- C_{ss} = Concentration of surrogate
- A_{ss} = Area of surrogate
- I_s = Concentration of internal standard
- A_{is} = Area of internal standard
- RRF = Relative response factor (from continuing calibration)

C.4 Percent Recovery

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

C.5 Matrix Spike Percent Recovery

$$Conc_{.MS} = \frac{SSR - SR}{SA} x100$$

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

C.6 Relative Percent Difference

$$RPD = \frac{|R_1 - R_2|}{-R_1, R_2} x100$$

where: R1 = First sample value (original)
R2 = Second sample value (duplicate)

C.7 Sample Quantitation Limit (SQL)

$$SQL = RL_{sow} x DF x \frac{SOW\ Weight}{Sample\ Weight} x \frac{SOW\ Aliquot}{Sample\ Aliquot} x \frac{1}{\%S}$$

where: RL_{SOW} = Required RL
DF = Dilution factor
%R = % solids (100 - % moisture)/100

C.8 Waters

$$\mu g/L = \frac{A_x x I_s x D_f}{A_{is} x RRF x V_o}$$

C.9 Soils (low level—dry weight basis)

$$\mu g/Kg = \frac{A_x x I_s}{A_{is} x RRF x W_s x D}$$

C.10 Soils (medium level—dry weight basis)

$$\mu g/Kg = \frac{A_x x I_s x V_t x 1000 x D_f}{A_{is} x RRF x W_s x V_a x D}$$

where:

A_x	=	Area of the characteristic ion of the compound being measured
A_{is}	=	Area of the characteristic ion of the internal standard
I_s	=	Amount of internal standard added (ng)
RRF	=	Daily response factor for compound being measured
V_o	=	Volume of water purged (mL)
W_s	=	Weight of sample
D	=	% solids
V_t	=	Volume of methanol (typically 10.0 mL)
D_f	=	Dilution factor
V_a	=	Volume of the aliquot of the methanol extract (µL) added to reagent water for purging

C.11 Relative Error

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

where:

x	=	True value for the calibration standard
x’	=	Measured concentration of calibration standard

C.12 Relative Standard Error

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

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

THIS PAGE INTENTIONALLY LEFT BLANK