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CP2-ES-5105/FR4

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

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

Date Issued—November 2025

U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

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

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APPROVALS

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

CP2-ES-5105/FR4

November 2025

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REVISION/CHANGE LOG				
Revision/ Change Letter	**Description of Changes**	**Pages Affected**	**Date of Revision/ Change**	**Approved By (signature on file)**
FR0	Bluesheet	All	11/14/2017	Signature on file
FR1	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
FR4	Revision to Section 4.2.1, update Appendix A, and other general revisions as needed.	All	11/24/2025	Signature on file

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CONTENTS

TABLES

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ACRONYMS

BNA	base/neutral and acid
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
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
ICV	initial calibration verification
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MB	method blank
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
m/z	mass-to-charge
N/A	not applicable
QAPP	quality assurance project plan
QC	quality control
QSM	quality systems manual
RL	reporting limit
RPD	relative percent difference
RRF	relative response factor
RRT	relative retention time
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
SQL	sample quantitation limit
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

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DEFINITIONS

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

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

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

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

Case—A finite, usually predetermined number of samples, that 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 Limit—The practical quantitation limit is defined as the lowest concentration of a contaminant that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation limit is typically several times higher than the method detection limit.

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

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

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

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

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

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

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

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

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—A compound unlikely to be found in a sample, is spiked into samples in a known amount before extraction or other processing, and is quantitated with the same procedures used to quantify other sample components. For semivolatile organic analysis and volatile organic analysis, surrogates are added to every sample, blank, 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 (GC/MS) 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 GC/MS 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 National Functional Guidelines for Organic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

1.2 APPLICABILITY

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

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

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

2. RESPONSIBILITIES

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

Table 1. Responsibilities for Data Validator and SMO

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

3. GENERAL INFORMATION

3.1 LEVELS OF LABORATORY DATA DELIVERABLES

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

Table 2. Required Laboratory Report Elements

Laboratory Report Elements*	Level I	Level II	Level III	Level IV
Cover/Signature Page/Executive Summary	✓	✓	✓	✓
Table of Contents	✓	✓	✓	✓
Laboratory Report Narrative	✓	✓	✓	✓
Method Summary		✓	✓	✓
Sample Summary/Sample Data Sheets	✓	✓	✓	✓
Shipping and Receiving Documents	✓	✓	✓	✓

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			✓	✓
GC Dual Column Identification Summary			✓	✓
Linear Ranges			✓	✓
Preparation Batch Log			✓	✓
Interference Check Standard Summary			✓	✓
Serial Dilution Summary			✓	✓
Cleanup Log			✓	✓
Standard/Reagent Traceability Log			✓	✓
Accreditation/Certification Summary			✓	✓
Raw Sample Data			✓	✓
Raw QC Data			✓	✓
Manual Integration Summary			✓	✓

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

3.2 STAGES OF VALIDATION

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

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

- **Stage 1 Validation**: A verification and validation based only on completeness and compliance of sample receipt condition checks. Client sample IDs and target analytes are verified against the COCs for completeness; sample conditions upon arrival at laboratory noted; sample preservation was appropriate and verified by the laboratory; holding times were met; concentrations and units were 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 (including LCSD and MSD), surrogates (organics), serial dilutions, post digestion spikes (as appropriate to the method) and any preparatory batch cleanup QC to assure that project requirements for analyte spike list, frequency, and QC limits are met.

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

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

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

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

3.3 DATA ASSESSMENT REVIEW

The data assessment review includes the following.

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

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

3.3.1 Data Verification/Contractual Screen

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

3.3.2 Data Validation

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

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

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

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

3.3.3 Data Assessment

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

3.3.4 Data Usability Assessment

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

4. DATA VERIFICATION AND VALIDATION INSTRUCTIONS

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

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

4.1 SAMPLE RECEIPT CONDITIONS

4.1.1 Chain-of-Custody

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

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

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

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

4.1.1.1 Data verification

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

4.1.1.2 Data validation

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

4.1.2 Holding Time, Temperature, and Sample Preservation

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

4.1.2.1 Deliverables

The following are deliverables.

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

4.1.2.2 Criteria

Table 3 provides current industry-accepted standards for sample preservation and hold times for 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 hydrochloric acid, or sodium bisulfate, or sulfuric acid, 0–6°C	14 days
	Water[a]	unpreserved, 0–6°C	7 days
	Soil (EnCores)	0–6°C	48 hours[b] 14 days
	Soil, sediment, other solids	0–6°C	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

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

Parameters	Matrix	Preservatives	Holding Times
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.

[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

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

4.1.2.4 Data validation

Holding Times

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

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

If the holding time is exceeded, 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 applied.

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 temperature and/or preservation issues.

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

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. Samples extracted and/or analyzed outside 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 received at elevated temperature (≤ 10°C) with correct preservative (if applicable).	J	UJ
4. Samples received at elevated temperature (>10°C) with correct preservative (if applicable).	*	*
5. Samples preserved improperly.	*	*

*Use professional judgment.

4.2 SAMPLE-RELATED QUALITY CONTROL RESULTS

4.2.1 Blanks

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

Method Blank

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

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

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

Equipment Rinsate Blank

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

4.2.1.1 Deliverables

The following are deliverables.

- MB report for each MB
- 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

An MB **shall** be considered contamination **if** one of the following occurs:

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

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

4.2.1.4 Data verification

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

4.2.1.5 Data validation

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, **then** the sample shall be evaluated against the blank with the highest concentration of the compound. Sample results must **NOT** be modified by subtracting blank values. When comparing blank results to analytical sample results, ensure that factors such as dilution and different sample weights have been taken into consideration.

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

If a compound was detected in the MB, **then** apply validation codes to data as follows.

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

- **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** both MB concentration and sample concentration are greater than the method detection limit (MDL) and less than or equal to the RL, **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×).

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, **then** 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.

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

Table 5. Blanks Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. MB **NOT** analyzed at the appropriate frequency.	R	Not applicable (N/A)
2. MB **NOT** the same matrix as the samples.	R	N/A
3. Sample result greater than RL and > 5×[a] blank result.	N/A	N/A
4. Sample result greater than RL and ≤ 5×[a] blank result.	J	N/A
5. Sample and blank results less than or equal to the RL.	U	N/A
6. Gross contamination.	R[b]	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.

4.2.2 Laboratory Control Sample/Laboratory Control Sample Duplicate

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

4.2.2.1 Deliverable

The following are deliverables.

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

4.2.2.2 Frequency

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

4.2.2.3 Criteria

The LCS **must** be analyzed and the LCS percent recovery (%R) **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, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a “L05” validation reason code to the affected data if a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.2.5 Data validation

Confirm that the LCS was analyzed (VOA) or prepared and analyzed (SVOA). **If** the SVOA LCS was analyzed only (i.e., not prepared), **then** it will provide limited value for method accuracy. The following guidance is suggested for qualifying sample data for which the associated LCS and/or LCSD does not meet the required criteria.

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

- **If** the LCS %R for an analyte ≥ 10% and less than the DoD/DOE QSM lower acceptance limit, **then** apply a “J” validation code to detected results and apply an “UJ” validation code to nondetected results.

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

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

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

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

Table 6. LCS Validation Qualification Guidance

	Validation 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. LCS %R > DoD/DOE QSM upper acceptance limit.	J	N/A
4. LCS %R ≥ 10% and < DoD/DOE QSM lower acceptance limit.	J	UJ
5. LCS %R < 10%.	J	R
6. LCS and LCSD RPD > 30%.	J	N/A
7. Analyte **NOT** spiked in LCS and/or 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 %R criteria are not satisfied, **then** there is difficulty in assessing whether the cause was due to method performance or matrix. To address this issue, LCS and/or LCSD are analyzed to verify method accuracy. **If** only the MS/MSD are affected, **then** a matrix effect is likely.

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

4.2.3.1 Deliverables

The following are deliverables for evaluating MS/MSD.

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

4.2.3.2 Frequency

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

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 acceptance limits, **then** 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 SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an “M05” validation reason code to the affected data if a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.2.3.5 Data validation

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

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

In the absence of either the MS/MSD or LCS/LCSD, it is unlikely that a complete evaluation of method precision and accuracy can be completed. In this case, at a minimum, sample results should be considered estimated quantities due to the inability 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.

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

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

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

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

- **If** poor spike recovery occurs in a sample whose concentration is > 4× the spiked amount, **then** professional and technical judgment should be used in whether qualification of data is warranted.

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

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

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

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

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

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

Table 7. MS/MSD Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. MS/MSD **NOT** analyzed at the appropriate frequency.	J*	UJ*
2. Analyte **NOT** spiked in MS/MSD.	R	R
3. MS %R > DoD/DOE QSM upper acceptance limit.	J	N/A
4. MS %R ≥ 10% and < DoD/DOE QSM lower acceptance limit.	J	UJ
5. MS %R < 10%.	J	R
6. MS/MSD RPD > 30%.	J	N/A

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

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

4.2.4 Duplicates

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

4.2.4.1 Deliverables

The following are deliverables.

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

4.2.4.2 Frequency

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

4.2.4.3 Criteria

The following are criteria for laboratory and field duplicates.

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

- For sample concentrations > 5× the RL, the RPD precision criteria for aqueous and solid laboratory duplicate samples **must** be within ± 25% for both VOA and SVOA analyses.

- For sample concentrations > 5× the RL, the RPD precision criteria for aqueous field duplicate samples **must** be within ± 25% for both VOA and SVOA analyses. The RPD precision criteria for solid field duplicate samples **must** be within ± 40% for both VOA and SVOA analyses.

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

4.2.4.4 Data verification

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

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

4.2.4.5 Data validation

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

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

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

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

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

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

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

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

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

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

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

Table 8. Laboratory and Field Duplicate Validation Qualification Guidance

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

NOTE: The above control limits are method requirements for matrix-specific duplicate samples. It should be noted that laboratory variability arising from the subsampling of nonhomogeneous matrices is a common occurrence; therefore, for technical review purposes only, regional policy or project DQOs may allow the use of less restrictive criteria (e.g., 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 VOA, surrogate standards are added to water matrices prior to GC/MS purge and for solid matrices before extraction. For SVOA, surrogate standards are added prior to the extraction for water and solid matrices.

4.2.5.1 Deliverables

The following are deliverables related to surrogate standards:

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

4.2.5.2 Frequency

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

4.2.5.3 Criteria

The surrogate %Rs are evaluated against the laboratory determined limits. DoD/DOE QSM Appendix C provides acceptance criteria that can be used.

4.2.5.4 Data verification

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

4.2.5.5 Data validation

Evaluate surrogate %Rs that exceed the acceptance criteria.

- **If** surrogates are not spiked in sample, **then** apply a "J" validation code to detected results and apply an "R" validation code to nondetected results.

Volatile Analysis

Table D.1 in Appendix D provides an example listing of common VOA surrogates and their associated target analytes. Surrogate association can differ by laboratory. It is always a best practice to confirm surrogate associations with the analytical laboratory prior to qualifying data. When applying validation qualification guidance below, apply validation codes to target analytes that are associated with the surrogate that is outside of acceptance criteria.

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

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

- **If** 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

SVOA compounds can be classified into two subcategories of compounds known as base/neutral and acid (BNA) extractable compounds. Phenolic compounds make up the acid extractables. Polynuclear aromatic compounds are a subset of the base/neutral compounds. Surrogate standards that represent the acid compounds include 2-fluorophenol, 2,4,6-tribromophenol, and phenol-d5. Surrogate standards that represent the base/neutral compounds include 2-fluorobiphenyl, nitrobenzene-d5, and terphenyl-d14 (or p-terphenyl-d14). Table D.2 in Appendix D provides an example listing of common SVOA acid surrogates and their associated target analytes. All other semivolatile compounds not found in Table D.2 are base/neutral compounds. Surrogate association can differ by laboratory. It is always a best practice to confirm surrogate associations with the analytical laboratory prior to qualifying data. When applying validation qualification guidance below, apply validation codes to target analytes that are associated with the surrogate that is outside of acceptance criteria.

- **If** surrogate %R is greater than the upper control limit, **then** apply a "J" validation code to detected results for applicable BNA fraction. No qualification is necessary for nondetected results.

- **If** surrogate %R ≥ 10% and less than the lower control limit, **then** apply a "J" validation code to detected results for the applicable BNA fraction and apply a "UJ" validation code to nondetected results for that fraction.

- **If** surrogate %R < 10%, **then** apply a "J" validation code to detected results for the applicable BNA 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.

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

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

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

Table 9. Surrogate Validation Qualification Guidance

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

*Use professional judgment and qualify only if the deviation indicates an adverse effect on data quality.

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 for the GC/MS performance check.

- Instrument performance check summary for each GC/MS system used
- Raw data (required for confirmation)

4.3.1.2 Frequency

The instrument performance check (also called a tuning 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 SW-846 Method 8260D or semivolatiles by EPA SW-846 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) if method performance is not adversely affected.

Table 10. VOA GC/MS 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

NOTE: 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. SVOA GC/MS Tuning Criteria

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

NOTES:

1. 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.
2. 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 (4,4’-DDE) and 4,4’-dichlorodiphenyldichloroethane (4,4’-DDD) 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

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

4.3.1.5 Data validation

Review the instrument performance check summary for VOA and SVOA analyses.

If GC/MS performance check is **NOT** performed at the proper frequency, **then** the data validators must use professional judgment to evaluate the integrity of the reported results. Data may require application of an “R” validation code.

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 in the evaluation of SVOA 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 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, **then NO** qualification of the data is necessary.

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 applying validation reason code "P06," **then** the data validator should use professional judgment in deciding the impact of the reported instrument performance of the data.

Evaluate the SVOA GC/MS performance check for the percent breakdown of 4,4'-DDT and chromatogram tailing.

- **If** 4,4'-DDT % breakdown > 20%, **then** apply an "R" validation code to associated results for 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE. No qualification is necessary for other compounds.

- **If** the tailing factor is > 2, **then** apply an "R" validation code to associated polycyclic aromatic hydrocarbon detected results and nondetected results.

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

Table 12. GC/MS Tuning Validation Qualification Guidance

Validation Step	Validation Qualification Guidance	
	Detects	**Nondetects**
1. GC/MS performance check **NOT** performed at the proper frequency.	*	*
2. Incorrect mass ion assignment.	R	R
3. 4,4'-DDT % breakdown > 20%.	R	N/A
4. Tailing factor > 2.	R	R
5. Instrument performance did **NOT** meet ion abundance criteria.	*	*

*Use professional judgment to qualify data.

4.3.2 Initial Calibration

Compliance requirements for satisfactory instrument calibration ensure that the instrument can produce 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.

The following subsections present the most common requirements for calibration information related to VOA/SVOA 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.

4.3.2.1 Deliverables

The following are deliverables for evaluating initial calibration.

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

4.3.2.2 Frequency

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

4.3.2.3 Criteria

The on-column standard concentrations and performance criteria for initial calibration include the following:

- Lowest concentration at the RL;
- Five levels minimum for linear model;
- Six levels minimum for quadratic model;
- Seven levels minimum for cubic model;
- Average response factor calibration: percent relative standard deviation (%RSD) ≤ 20%; and
- Coefficient of determination (r^2) for linear and quadratic calibration curves should be ≥ 0.99.

4.3.2.4 Data verification

Verify the presence of required reporting forms. **If** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a "C07" validation reason code to affected data if a noncorrectable problem has occurred **and** the problem has 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 exhibiting poor response listed in Table 13). 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 13. VOA and SVOA Target Compounds Exhibiting Poor Response

VOA Compounds		SVOA 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 %RSD > 20% for a target analyte, **then** apply a "J" validation code to detected results and apply a "UJ" validation code to nondetected results, unless the laboratory uses Option 1 or Option 2 as detailed below.

Nonlinearity in the calibration curve is indicated **if** the %RSD > 20%. The laboratory may elect to calculate a linear or quadratic calibration curve. The linear and nonlinear (quadratic) calibration curve criteria are listed below.

- **Option 1**: linear least squares regression for each analyte: $r^2 \geq 0.99$; or
- **Option 2**: nonlinear (quadratic) regression for each analyte: $r^2 \geq 0.99$.

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 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.

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

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

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

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

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

- **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 for each sample matrix, **then** apply an "R" validation code to the detected and nondetected results.

- **If** less than the required minimum number of calibration standards were used, **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 code 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 14 summarizes data validation qualification guidance for the initial calibration.

Table 14. Initial Calibration Validation Qualification Guidance

	Validation Qualification Guidance	
Validation Step	**Detects**	**Nondetects**
1. Compounds' average RRF < 0.05 (or < 0.01*).	J	R
2. %RSD > 20%.	J	UJ
3. $r^2 > 0.90$ and $r^2 < 0.99$.	J	UJ
4. $r^2 < 0.90$.	J	R
5. %RE > 20% (mid-range) or %RE > 50% (low level) of the calibration.	J	UJ
6. %RSE > 30%.	J	UJ
7. Sample concentration exceeds calibration range.	J	N/A
8. Target analytes not calibrated for each sample matrix.	R	R
9. Less than the required minimum calibration standards used.	R	R
10. Lowest calibration standard greater than RL.	J	UJ

*Poor response compounds (Table 13).

4.3.3 Initial and Continuing Calibration Verification

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

4.3.3.1 Deliverables

The following are deliverables for evaluating ICVs and CCVs.

- Continuing calibration (ICV/CCV) summary for each GC/MS 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 CCV **must** be analyzed prior to and at the end of sample analysis.

4.3.3.3 Criteria

The performance criteria for ICV/CCV include the following:

- Mid-level standard run every 12 hours;
- Percent difference (%D) ≤ ± 20% for ICV or opening CCV; and
- %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 SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem. Apply a "C07" validation reason code to the affected data if a noncorrectable problem has occurred **and** the problem has an adverse effect on data quality.

4.3.3.5 Data validation

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.

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 13), **then** apply a "J" validation code to detected results with acceptable mass spectral identification. Use professional judgment when qualifying 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 15 summarizes data validation qualification guidance for issues with the ICV/CCV.

Table 15. ICV/CCV Performance Validation Qualification Guidance

	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 exceeds ± 20% but does **NOT** exceed ± 50%.	J	UJ
4. The %D for ICV or opening CCV exceeds ± 50%.	R	R
5. The %D for closing CCV exceeds ± 50% but does **NOT** exceed ± 80%.	J	UJ
6. The %D for closing CCV exceeds ± 80%.	R	R
7. RRF < 0.05 (or < 0.01 for compounds in Table 14) and %D exceeds ± 20%.	J	*

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

4.3.4 Internal Standards

Internal standards are used to ensure that GC/MS sensitivity and response are stable during analysis.

Appendix E provides an example listing of VOA and SVOA internal standards and their associated target analytes. Internal standard association can differ by laboratory. It is always a best practice to confirm internal standard associations with analytical laboratory prior to qualifying data.

4.3.4.1 Deliverables

The following are deliverables for evaluating internal standards.

- 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 RT 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 peak area response of each internal standard compound in all samples and blanks must be within the inclusive range of 50–200% of the peak 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 to have the laboratory provide the missing information. **If** the issue cannot be resolved by the analytical laboratory, **then** it is considered a noncorrectable problem. Apply an “I07” validation reason code to affected data if a noncorrectable problem has occurred and the problem has 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 response %D ≥ 20% and < 50%, **then** apply a “J” validation code to associated detected results and apply a “UJ” validation code to associated nondetected results.

- **If** peak area response %D > 200%, **then** apply a “J” validation code to associated detected results. No qualification is necessary for associated nondetected results.

- **If** peak area response %D < 20%, **then** apply an “R” validation code to detected and nondetected results.

- **If** internal standard RTs vary by more than ± 10 seconds (between the sample internal standard and calibration internal standard), 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 16 summarizes data validation qualification guidance for issues with the internal standards.

Table 16. Internal Standard Validation Qualification Guidance

	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. Peak area response %D < 20%	R	R
4. %D ≥ 20% and %D < 50%	J	UJ
5. %D > 200%	J	N/A

[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 should be greater than or equal to the lowest calibration standard used in the initial calibration.

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

4.4.1.1 Deliverables

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

- Sample summary/sample data sheets

4.4.1.2 Frequency

RLs or SQLs are reported for all compounds.

4.4.1.3 Data verification

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

4.4.1.4 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 for evaluating TICs.

- 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** they are not provided, **then** contact the SMO to have the laboratory provide the missing information. **If** the issue cannot be resolved with the analytical laboratory, **then** it is considered a noncorrectable problem **and** should be noted 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 ± 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 RT. 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, **then** 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 RRT.

- **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 GC column bleed artifacts)
- Diethyl ether (1,1-oxybisethane)
- Hexane
- 1,1,2-Trichloro-1,2,2-trifluoroethane (trichlorotrifluoroethane 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)

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.

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APPENDIX A

DATA VALIDATION CODES AND DATA VALIDATION REASON CODES

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

Data Validation Codes

U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
NJ	Presumptively present at an estimated quantity [use with tentatively identified compounds (TICS) only].
UJ	Analyte, compound, or nuclide not detected above the reported detection limit, and the reported detection limit is approximated due to quality deficiency.
R	Result rejected by validator.
=	Validated result, no additional qualifier necessary.
X	Not validated; Refer to the RSLTQUAL field for more information.

Data Validation Reason Codes

Blanks

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

Calibration

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

Calibration (continued)

C08	Calibration not performed
C09	Chemical resolution criteria were not satisfied
C10	Calibration standard matrix not the same as sample matrix
C11	Compounds quantitated against inappropriate standard or standard concentration level
C12	Compound quantitated against inappropriate ion
C13	Calibration factor relative standard deviation criteria were not satisfied
C14	Retention time of compound outside window
C15	Initial calibration percent recovery (%R) was below lower acceptance limit
C16	Initial calibration %R was above upper acceptance limit
C17	Initial calibration curve fit was < 0.995
C18	Inappropriate standard concentrations
C19	Continuing calibration %R was below the lower acceptance limit
C20	Continuing calibration %R was above the upper acceptance limit
C21	Contract-required detection limit (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

Holding Times/Preservation (continued)

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

Internal Standards

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

Laboratory Control Sample (LCS)

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

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

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

Instrument Performance

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

Quantitation

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

Quantitation (continued)

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

Surrogates

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

Instrument Tuning

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

Pesticide Sample Cleanup

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

Cleanup

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

Cleanup (continued)

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

Dilutions

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

Radiochemical Yield

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

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APPENDIX B

QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

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B.1. QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

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

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

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

Data Quality Indicator	Effect on Sample Data
GC/MS tuning	Compound identification
Initial calibration	Identification and quantitation
ICV/CCV	Quantitation
Surrogate standards	Positive or negative bias
Internal standards	Positive or negative bias
Method blank	Positive bias
LCS/LCSD	Method bias and precision
MS/MSD	Positive or negative bias and precision

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

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APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

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C.1. RULES, CALCULATIONS, AND EQUATIONS

Rounding Rules

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

Calculations/Equations

C.1 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)

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

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

C.8 Waters

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

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

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

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

$$\mu g/Kg = \frac{A_x x I_s x V_t x1000x D_f}{A_{is} xRRFx W_s x V_a xD}$$

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

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APPENDIX D

SURROGATE AND TARGET ANALYTE ASSOCIATIONS

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D.1. SURROGATE AND TARGET ANALYTE ASSOCIATIONS

Table D.1. VOA Surrogates and Associated Target Analytes

VOA Surrogate	Associated Target Analytes		
1,2-Dichloroethane-d4	1,1,1-Trichloroethane 1,1-Dichloroethane 1,1-Dichloroethene 1,1-Dichloropropene 1,2-Dichloroethane 1,2-Dichloropropane 1,4-Dioxane 2-Butanone 2-Chloro-1,3-butadiene 2-Chloroethylvinyl ether 2-Pentanone 2,2-Dichloropropane 2-Nitropropane Acetone Acetonitrile Acrolein Acrylonitrile Allyl chloride Benzene Bromochloromethane	Bromodichloromethane Bromomethane Carbon disulfide Carbon tetrachloride Chloroethane Chloromethane Chloroform *cis*-1,2-Dichloroethene *cis*-1,3-Dichloropropene Cyclohexane Cyclohexene Dibromomethane Dichlorodifluoromethane Ethyl acetate Ethyl ether Ethyl *tert*-butyl ether Iodomethane Isobutyl alcohol Isopropyl alcohol	Isopropyl ether Methacrylonitrile Methyl acetate Methyl methacrylate Methyl *tert*-amyl ether Methylcyclohexane Methylene chloride n-Butyl alcohol n-Hexane Propionitrile *tert*-Butyl methyl ether *tert*-Butyl alcohol Tetrahydrofuran *trans*-1,2-Dichloroethene Trichloroethene Trichlorofluoromethane Trichlorotrifluoroethane Vinyl acetate Vinyl chloride
Toluene-d8	1,1,2-Trichloroethane 1,1,1,2-Tetrachloroethane 1,2-Dibromoethane 1,3-Dichloropropane 2-Hexanone 4-Methyl-2-pentanone	Chlorobenzene Dibromochloromethane Ethylbenzene Ethyl methacrylate m,p-Xylenes	o-Xylene Styrene Tetrachloroethene Toluene *trans*-1,3-Dichloropropene
Bromofluorobenzene	1-Chlorohexane 1,1,2,2-Tetrachlorethane 1,2-Dibromo-3-chloropropane 1,2-Dichlorobenzene 1,2,3-Trichlorobenzene 1,2,3-Trichloropropane 1,2,4-Trichlorobenzene 1,2,4-Trimethylbenzene 1,3-Dichlorobenzene 1,3,5-Trimethylbenzene	1,4-Dichlorobenzene 2-Chlorotoluene 4-Chlorotoluene 4-Isopropyltoluene Benzyl chloride bis(2-Chloro-1-methylethyl) ether Bromobenzene Bromoform *cis*-1,4-Dichloro-2-butene Cyclohexanone	Isopropylbenzene Hexachlorobutadiene n-Butylbenzene n-Propylbenzene Naphthalene Pentachloroethane *sec*-Butylbenzene *tert*-Butylbenzene *trans*-1,4-Dichloro-2-butene

Table D.2. SVOA Acid Surrogates and Associated Target Analytes

SVOA Acid Surrogates	Associated Target Analytes	
2-Fluorophenol 2,4,6-Tribromophenol Phenol-d5	2-Chlorophenol 2-Nitrophenol 2,3,4,6-Tetrachlorophenol 2,4-Dichlorophenol 2,4-Dimethylphenol 2,4-Dinitrophenol 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol 2,6-Dichlorophenol	2-Methyl-4,6-dinitrophenol 4-Chloro-3-methylphenol 4-Nitrophenol Benzoic acid m,p-Cresols o-Cresol Pentachlorophenol Phenol

APPENDIX E

INTERNAL STANDARDS AND TARGET ANALYTE ASSOCIATIONS

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Table E.1. VOA Internal Standards and Associated Target Analytes

VOA Internal Standards			
Fluorobenzene		**Chlorobenzene-d5**	**1,4-Dichlorobenzene-d4**
1,1,1-Trichloroethane	Dibromomethane	1,1,2-Trichloroethane	1-Chlorohexane
1,1-Dichloroethane	Dichlorodifluoromethane	1,1,1,2-Tetrachloroethane	1,1,2,2-Tetrachlorethane
1,1-Dichloroethene	Ethyl acetate	1,2-Dibromoethane	1,2-Dibromo-3-chloropropane
1,1-Dichloropropene	Ethyl ether	1,3-Dichloropropane	1,2-Dichlorobenzene
1,2-Dichloroethane	Ethyl *tert*-butyl ether	2-Hexanone	1,2,3-Trichlorobenzene
1,2-Dichloropropane	Iodomethane	4-Methyl-2-pentanone	1,2,3-Trichloropropane
1,4-Dioxane	Isobutyl alcohol	Chlorobenzene	1,2,4-Trichlorobenzene
2-Butanone	Isopropyl alcohol	Dibromochloromethane	1,2,4-Trimethylbenzene
2-Chloroethylvinyl ether	Isopropyl ether	Ethylbenzene	1,3-Dichlorobenzene
2-Chloro-1,3-butadiene	Methyl acetate	Ethyl methacrylate	1,3,5-Trimethylbenzene
2-Nitropropane	Methyl methacrylate	m,p-Xylenes	1,4-Dichlorobenzene
2-Pentanone	Methyl tert-amyl ether	o-Xylene	2-Chlorotoluene
2,2-Dichloropropane	Methacrylonitrile	Styrene	4-Chlorotoluene
Acetone	Methylcyclohexane	Tetrachloroethene	4-Isopropyltoluene
Acetonitrile	Methylene chloride	Toluene	Benzyl chloride
Acrolein	n-Butyl alcohol	*trans*-1,3-Dichloropropene	bis(2-Chloro-1-methylethyl) ether
Acrylonitrile	n-Hexane		Bromobenzene
Allyl chloride	Propionitrile		Bromoform
Benzene	*tert*-Butyl alcohol		*cis*-1,4-Dichloro-2-butene
Bromochloromethane	*tert*-Butyl methyl ether		Cyclohexanone
Bromodichloromethane	*trans*-1,2-Dichloroethene		Hexachlorobutadiene
Bromomethane	Tetrahydrofuran		Isopropylbenzene
Carbon disulfide	Trichloroethene		n-Butylbenzene
Carbon tetrachloride	Trichlorofluoromethane		n-Propylbenzene
Chloroethane	Trichlorotrifluoroethane		Naphthalene
Chloromethane	Vinyl acetate		Pentachloroethane
Chloroform	Vinyl chloride		*sec*-Butylbenzene
cis-1,2-Dichloroethene			*tert*-Butylbenzene
cis-1,3-Dichloropropene			*trans*-1,4-Dichloro-2-butene
Cyclohexane			
Cyclohexene			

Table E.2. SVOA Internal Standards and Associated Target Analytes

SVOA Internal Standard	Associated Target Analytes		
1,4-Dichlorobenzene-d4	1,2-Dichlorobenzene	Benzyl alcohol	N-Nitrosodiethylamine
	1,3-Dichlorobenzene	bis(2-Chloro-1-methylethyl) ether	N-Nitrosodipropylamine
	1,4-Dichlorobenzene	bis(2-Chloroethyl) ether	N-Nitrosomethylethylamine
	1,4-Dioxane	Ethyl methacrylate	N-Nitrosomorpholine
	2-Butoxyethanol	Ethyl methanesulfonate	N-Nitrosopyrrolidine
	2-Chlorophenol	Hexachloroethane	o-Cresol
	2-Ethoxyethanol	m,p-Cresols	o-Toluidine
	2-Picoline	Methyl methacrylate	p-Benzoquinone
	Acetophenone	Methyl methanesulfonate	Pentachloroethane
	Aniline	n-Decane	Phenol
	Benzaldehyde	N-Methyl-N-nitrosomethylamine	Pyridine

Table E.2. SVOA Internal Standards and Associated Target Analytes (Continued)

SVOA Internal Standard	Associated Target Analytes
Naphthalene-d8	1,2,4-Trichlorobenzene 1-Methylnaphthalene 2,4-Dichlorophenol 2,4-Dimethylphenol 2,6-Dichlorophenol 2-Methylnaphthalene 2-Nitrophenol 4-Chloro-3-methylphenol 4-Chloroaniline a,a-Dimethylphenethylamine alpha-Terpineol Benzoic acid bis(2-Chloroethoxy)methane Caprolactam Hexachlorobutadiene Hexachloropropene Isophorone Naphthalene Nitrobenzene N-Nitrosodi-n-butylamine N-Nitrosopiperidine p-Phenylenediamine Safrole Sulfolane Triethylphosphorothioate
Acenaphthene-d10	1,1-Biphenyl 1,2,4,5-Tetrachlorobenzene 1,4-Dinitrobenzene 1,4-Naphthoquinone 1-Naphthylamine 2,3,4,6-Tetrachlorophenol 2,3-Dichloroaniline 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol 2,4-Dinitrophenol 2,4-Dinitrotoluene 2,6-Dinitrotoluene 2-Chloronaphthalene 2-Naphthylamine 4-Chlorophenylphenylether 4-Nitrophenol 5-Nitro-o-toluidine Acenaphthene Acenaphthylene Dibenzofuran Diethylphthalate Dimethylphthalate Fluorene Hexachlorocyclopentadiene Isosafrole m-Dinitrobenzene m-Nitroaniline o-Nitroaniline Pentachlorobenzene p-Nitroaniline Thionazine Tributylphosphat
Phenanthrene-d10	2-Methyl-4,6-dinitrophenol 1,2-Diphenylhydrazine 1,3,5-Trinitrobenzene 4-Aminobiphenyl 4-Bromophenylphenylether 4-Nitroquinoline-1-oxide Anthracene Atrazine Benzidine Carbazole *cis*-Diallate Diallate Dimethoate Di-n-butylphthalate Dinoseb Diphenylamine Disulfoton Fluoranthene Hexachlorobenzene Isodrin Methapyrilene Methyl parathion n-Octadecane Parathion Pentachloronitrobenzene Pentachlorophenol Phenacetin Phenanthrene Phorate Prometon Pronamide Pyrene Sulfotepp *trans*-Diallate
Chrysene-d12	2-Acetylaminofluorene 3,3’-Dichlorobenzidine 3,3’-Dimethylbenzidine Aramite Benzo(a)anthracene bis(2-Ethylhexyl)phthalate Butylbenzylphthalate Chlorobenzilate Chrysene Di-n-octylphthalate Famphur Kepone Methoxychlor Methylenebis(2-chloroaniline) p-(Dimethylamino)azobenzene
Perylene-d12	3-Methylcholanthrene 7,12-Dimethylbenz(a)anthracene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(ghi)perylene Benzo(k)fluoranthene Dibenzo(a,e)pyrene Dibenzo(a,h)anthracene Hexachlorophene Indeno(1,2,3-cd)pyrene