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

FOUR RIVERS NUCLEAR PARTNERSHIP, LLC

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

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U.S. DEPARTMENT OF ENERGY
Office of Environmental Management

Prepared by
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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
Paducah Gasesous Diffusion Plant,
Paducah, Kentucky

CP2-ES-5105/FR2

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ACRONYMS

CCV	continuing calibration verification
CFR	*Code of Federal Regulations*
CLP	Contract Laboratory Program
COC	chain of custody
DQO	data quality objective
EB	equipment blank
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
FB	field blank
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
QAPP	quality assurance project plan
QC	quality control
RF	response factor
RL	reporting limit
RDL	required detection limit
RPD	relative percent difference
RRT	relative retention time
RRF	relative response factor
RSD	relative standard deviation
SDG	sample delivery group
SMO	Sample Management Office
SOW	statement of work
SPCC	system performance check compound
SQL	sample quantitation limit
SVOA	semivolatiles analysis
TIC	tentatively identified compound
VOA	volatiles analysis
%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation

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DEFINITIONS

NOTE 1: Qualifier definitions are listed in Appendix A.

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

AFFECTED SAMPLE RESULT—A sample result is considered to be affected when it is significantly influenced by a quality deficiency and is qualified accordingly through analytical data validation.

ANALYTICAL DATA VALIDATION—Analytical 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.

ANALYTICAL DATA VERIFICATION—Analytical 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.

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.

BROMOFLUOROBENZENE—An instrument performance check compound for volatile organics analysis by gas chromatography/mass spectrometry (GC/MS).

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

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

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

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 revealed during verification are those deficiencies that can be addressed by obtaining additional information from the laboratory. Correctable problems revealed during validation are those deficiencies with analyses that can be solved either by a second preparation and/or by analysis of a sample.

DATA QUALITY OBJECTIVE (DQO)—DQOs are qualitative and quantitative statements derived from the outputs of each step of the DQO process that specify the study objectives, domain, limitations, the most appropriate type of data to collect, and specify the levels of decision error that will be acceptable for the decision.

DATA QUALITY OBJECTIVES PROCESS—The DQO 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 DQO process enables planners to focus their planning efforts by specifying the use of the data (the decision), the decision criteria (action level), and the decision maker's acceptable decision error rates.

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 GC/MS instrument against a traceable standard of known identity and quantity. This standardization prevails until such time as analytical conditions are deemed out of acceptable control limits.

INTERNAL STANDARD—Internal standards are nontarget compounds added to every volatile organic analysis (VOA) and semivolatile organic analysis (SVOA) 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 (LCS)—The LCS is a control sample of known composition. Aqueous and solid LCSs are analyzed using the same preparation, reagents, and method employed for field samples.

LABORATORY DUPLICATE—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 (MS)—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 (MB)—The MB 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 MB is to monitor the presence of contamination of the analyte of interest in the sample preparation and analysis processes.

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

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 (RPD)—RPD 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 (RSD)—RSD 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 (RDL)—The RDL is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

REPORTING LIMIT (RL)—The RL is a contractually specified detection limit that, under typical analytical circumstances, should be achievable.

SAMPLE DELIVERY GROUP (SDG)—An SDG 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 SDG.

SAMPLE QUANTITATION LIMIT (SQL)—SQLs are detection limits based on the RDL, 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 (SOW)—The validation SOW is a document prepared to function as the mechanism by which validation requirements are communicated from the project to the validation organization.

SURROGATE—For semivolatiles and volatiles, surrogates are non-target standard compounds added to every blank, sample matrix spike, matrix spike duplicate and standard used to evaluate analytical efficiency by measuring percent recovery. SVOA surrogates are brominated, fluorinated, or isotopically labeled compounds similar to the compounds of interest in chemical composition. VOA surrogates are brominated or deuterated compounds. Surrogates are not expected to be present in environmental media.

SYSTEM PERFORMANCE CHECK COMPOUND (SPCC)—Compounds used to establish the calibration of an instrument for the SW-846 analytical methodologies applied to VOA and SVOA.

TENTATIVELY IDENTIFIED COMPOUND (TIC)—TICs 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.

TURN-AROUND TIME—Turn-around 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 QUALIFIER—A qualifier is an alphabetic character physically or electronically associated with a discrete sample result during validation due to a data quality deficiency, which provides guidance in data usability.

VALIDATION STATEMENT OF WORK—The validation SOW is a document prepared to function as the mechanism by which validation implementation requirements are communicated from the project to the validation organization.

VOLATILE ORGANICS ANALYSIS—Method based on the purge and trap technique for organic compound analysis.

1. INTRODUCTION

1.1 PURPOSE, SCOPE, AND APPLICATION

1.1.1 Purpose

This plan defines the minimum requirements, responsibilities, and methodology for the volatile organic analysis (VOA) and semivolatile organic analysis (SVOA) data verification and validation processes for evaluating analytical data generated using gas chromatography/mass spectrometry (GC/MS).

This plan provides requirements for developing and implementing a validation methodology for volatiles and semivolatiles Contract Laboratory Program (CLP) and SW-846 (8260 and 8270) analytical methods primarily for analytes in aqueous and soil/sediment matrices. It is flexible enough to allow evaluation of data usability for project-specific data quality objectives (DQOs). Data produced by analytical methods for which this plan provides limited guidance (i.e., Method 8011, Appendix A of 40 *CFR* Part 136, *Protection of Environment*, Appendix A, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," or "Superfund Low Concentration Statement of Work" methods) may necessitate 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 contained herein, data validators are advised to seek guidance in the specific method employed and/or from other industry standards. Examples include the U.S. Environmental Protection Agency (EPA), CLP, National Functional Guidelines for Organic Data Review, EPA Regional Data Validation Guidance, and subject matter experts within the industry.

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

1.1.2 Scope and Application

This plan applies to volatile and semivolatile data verification and validation activities performed by the Sample Management Office (SMO) or its subcontractors.

2. RESOURCES

- Analytical Method
- Laboratory SOW
- Data Validation SOW
- Project-Specific QAPP

3. PREPERFORMANCE ACTIVITIES

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

4. GENERAL INFORMATION

4.1 REQUIRED ELEMENTS OF REVIEW AND VALIDATION

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

Table 1. Required Elements of Review and Validation

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

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

Report Elements to be Reviewed*	Level I	Level II	Level III	Level IV
(Quant + Chro Follows Each Form Set)				x
QC DATA			x	x
Tune			x	x
Blank Form I			x	x
Blank Quant Rpt + Chro + Spectra				x
LCS/LCSD Form I			x	x
LCS/LCSD Quant Rpt + Chro + Spectra				x
MS/MSD Form I			x	x
MS/MSD Quant Rpt + Chro + Spectra				x
GEL Permeation Data				x
Florisil Data				x
Logs—Instrument, Prep, Standard			x	x
CLP-Like Inorganics				
Cover Page			x	x
Sample Forms (I) (CLP-like)			x	x
Calibration + QC Forms (exp.: II–XIV)			x	x
Instrument Data				x
Preparation Data				x
SHIPPING/RECEIVING DOCUMENTS				
Internal COC (if required)			x	x
Interlab COC (where applicable)			x	x
Client COC	x	x	x	x
Sample Receipt Checklist	x	x	x	x

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

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

4.2 DATA VERIFICATION REQUIREMENTS

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

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

Data verification, at the project level, is conducted by an SMO representative to expedite the review process. If data verification is conducted independently of the data validator, it includes two activities. The first activity entails inventory of the data package to ensure compliance with the contract and SOW, in terms of the required deliverables. The second activity entails various checks of the data quality to determine the need for qualification. This process is commonly referred to as the "contractual screen" and is the beginning of the data validation process in that it encompasses the review of the Level I and some

Level II validation elements identified in Table 1 above. The data verifier will qualify data based on the review and validation elements in accordance with Section 5 of this plan. If the data set is being reviewed and validated at the Level III or IV requirements, then the data verifier will provide a copy of the data verification checklist to the data validator to expedite the validation process, or the data validator will perform both the data verification and the data validation processes.

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

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

4.3 ANALYTICAL DATA VALIDATION REQUIREMENTS

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

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

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

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

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

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

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

5. PROCEDURE

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

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

5.1 DATA VALIDATION STRATEGY AND SOW DEVELOPMENT

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

5.2 CUSTODY OF SAMPLES AND SAMPLE DOCUMENTATION

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

demonstrated by the series of signatures denoting sample holders, could jeopardize the legal and/or technical defensibility of associated sample data.

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

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

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

5.2.1 Data Verification

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

5.2.2 Data Validation

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

Custody of Samples	**Yes**	**No**	**N/A**
1. Does the data verification checklist or associated attachments in the data report indicate that samples are traceable?			

5.3 HOLDING TIME, TEMPERATURE, AND SAMPLE PRESERVATION

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

5.3.1 Deliverables

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

5.3.2 Criteria

Table 2 provides current industry-accepted standards for sample preservation and holding times for volatile and semivolatile parameters. In all cases, the data verifier or validator shall always follow the most current methodology guidance for sample holding time, temperature, and preservation requirement.

Table 2. Holding Time and Sample Preservation Criteria

Parameters	Matrix	Preservatives	Holding Times
Volatile Organics	Water*	pH < 2 with HCl, H_2SO_4, or solid $NaHSO_4$, 0–6°C	14 days
	Water	0–6°C	7 days
	Soil (EnCores)	0–6°C	48 hours** 14 days
	Soil, sediment, other solids	0–6°C	14 days
		SW-5035 - low concentration pH < 2 with $NaHSO_4$, 0–6°C	14 days
		SW-5030 - high concentration Methanol, 0–6°C	14 days
Semivolatile (Extractable) Organics	Water	0–6°C	7 days** 40 days***
	Soil, sediment, other solids	0–6°C	14 days** 40 days***

*Aqueous samples known to contain carbonates or being analyzed for select target analytes should be collected unpreserved to minimize effervescence or destruction of target analyte upon acidification. These samples are chilled to 0–6°C and have a seven-day hold period.
**Time from collection of sample to extraction.
***Time from extraction to completion of analysis.

5.3.3 Data Verification

The data verifier shall verify the presence of the pertinent COC forms in laboratory deliverables. If information is missing, the data verifier will seek to obtain field documentation from the sampler and/or the contract laboratory to determine if the omission affects sample integrity. Upon receipt, this information will be placed in the data package for delivery to the data validator. If missing information cannot be obtained or reconstructed from field notes, COCs, etc., the data verifier will note omitted information on the data verification checklist as noncorrectable.

5.3.4 Data Validation

5.3.4.1 Holding times

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

If the elapsed time falls within the prescribed holding time, no actions will be taken and no qualification assigned.

If holding time is exceeded, qualify as follows:

- If the holding time is exceeded by a factor of < 2, qualify detected results as "J" and nondetected results as "UJ."

- If the holding time is grossly exceeded by a factor > 2, qualify detected results as estimated "J" and nondetected results as rejected "R."

5.3.4.2 Temperature/preservation

Review laboratory receiving records to determine if samples were received at the appropriate temperature and that proper preservative addition has resulted in the appropriate pH adjustment(s). If records demonstrate samples were received by the laboratory at the proper temperature and with the appropriate pH adjustment, no action is warranted.

If temperatures are exceeded and/or pH adjustment is incorrect, qualify as follows:

- If samples are received without the proper pH adjustment and not analyzed within an acceptable time frame for an unpreserved sample, qualify detected results as estimated "J" and nondetected results as "UJ" or rejected "R." Professional judgment will need to be used to determine the effect of the improper pH and whether the nondetect result should be qualified "UJ" or "R."

- If samples are received at elevated temperature (6°C < sample temperature < 10°C) but have received the proper pH adjustment, qualify detected results as "J" and nondetected results as "UJ," indicating the results are estimated. If sample temperatures upon receipt are > 10°C, the data validator must evaluate the integrity of the reported concentrations and the data may require qualification of "R."

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

- If samples are received with air bubbles in the vials, qualify detected results as estimated "J" and nondetected results as rejected "R."

Holding Times and Sample Preservation				Qualification Guidance	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Does the data verification checklist indicate that all samples were analyzed within the appropriate holding time?				J	UJ/R*
2. Were all samples preserved properly?				J	UJ/R

*Qualify "R" only if holding time has been grossly exceeded either on the first analysis or upon reanalysis.

5.4 GC/MS PERFORMANCE CHECK

5.4.1 Deliverables

- CLP Form V-VOA, Form V-SV or equivalent for SW-846 methods for each GC/MS system used
- Raw data (required for confirmation)

5.4.2 Frequency

The instrument performance check must be analyzed at the beginning of each 12-hour period during which samples and/or standards are analyzed. If different instruments are used on samples in a similar case, the performance check(s) must be analyzed at this frequency as well.

5.4.3 Criteria

Table 3 and Table 4 present ion abundance criteria for both CLP and SW-846 methods. The criteria in these tables are intended to be used as default criteria for quadruple instrumentation if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected.

Table 3. Volatile Organic GC/MS Tuning Criteria

m/z	Ion Abundance Criteria (CLP SOW 5/99–OLM04.2)	Ion Abundance Criteria (SW-846 Method 8260B)*
50	8.0–40.0% of m/z 95	15.0–40.0% of m/z 95
75	30.0–66.0% of m/z 95	30.0–60.0% of m/z 95
95	Base peak, 100% relative abundance	Base peak, 100% relative abundance
96	5.0–9.0% of m/z 95	5.0 –9.0% of m/z 95
173	< 2.0% of m/z 174	< 2.0% of m/z 174
174	50.0 –120.0% of m/z 95	> 50.0% and < 120% of m/z 95
175	4.0 –9.0% of m/z 174	5.0 –9.0% of m/z 174
176	93.0 –101.0% of m/z 174	> 95.0%, but < 101.0% of m/z 174
177	5.0 –9.0% of m/z 176	5.0 –9.0% of m/z 176

*All ion abundances must be normalized to mass-to-charge (m/z) 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

Table 4. Semivolatile Organic GC/MS Tuning Criteria

m/z	Ion Abundance Criteria (CLP SOW 5/99–OLM04.2)	Ion Abundance Criteria (SW–846 Method 8270D)
51	30.0–80.0% of m/z 95	10.0–80.0% of m/z 198
68	< 2.0% of m/z 69	< 2.0% of m/z 69
69	Present	Present
70	< 2.0% of m/z 69	< 2.0 of m/z 69
127	25.0–75.0% of m/z 198	10.0–80.0% of m/z 198
197	< 1.0% of m/z 198	< 2 0% of m/z 198
198	Base peak, 100% relative abundance	Base peak, or > 50.0% of m/z 442
199	5.0–9.0% of m/z 198	5.0–9.0% of m/z 198
275	10.0–30.0% of m/z 198	10.0–60.0% of m/z 198
365	> 0.75% of m/z 198	> 1.00% of m/z 198
441	Present, but < m/z 443	Present, but < 24.0% of m/z 442
442	40.0–110.0% of m/z 198	Base peak, or > 50% of mass 198
443	15.0–24.0% of m/z 442	15.0 –24.0% of m/z 442

*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 be up to 100% that of m/z 198.

5.4.4 Data Verification

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

5.4.5 Data Validation

The data validator shall review the data verification checklist to confirm the presence of the appropriate forms (Form V) for VOA and SVOA analyses. If the data verification checklist notes that the GC performance forms are missing and these occurrences cannot be resolved with the contract laboratory, they are considered noncorrectable problems. Place qualifier code “P05” on the affected data if noncorrectable deliverable deficiencies have occurred; qualify only if the deviation indicates an adverse effect on data quality.

If mass assignment is in error (such as m/z 199 is indicated as the base peak for SVOA analysis, rather than m/z 198), qualify all results “R.”

The following ion abundances always 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 criteria for critical or noncritical ion-abundances are not met. Guidance to aid the application of evaluation of semivolatile compounds is as follows:

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

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

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

The following ion abundances are of minor importance:

- Volatile: m/z 50 and 75
- Semivolatile: m/z 51, 127, and 275

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

If it is found that the laboratory made only minor calculation errors that do not affect the data quality, no qualification of the data is required.

If data is reported outside of the 12-hour clock of the instrument performance check, the data shall be reported as estimated “J” or “UJ” and a qualification code of “P06” assigned to the results.

If m/z ratios are not within the ion abundance criteria given within Tables 3 and 4, using the criteria indicated in the preceding paragraphs and using qualification code “P06,” the data validator should use professional judgment in deciding the impact of the reported instrument performance of the data.

GC/MS Performance Check				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Has the GC/MS instrument performance check been performed at the proper frequency?				*	*
2. Do all instrument performance checks satisfy ion abundance criteria?				Refer to Table 3 and Table 4 in Section 5.4 or the method being reviewed	
3. Does the raw data show proper averaging of scans? (Level IV validation only)				Refer to step 5.4.5 or the method being reviewed	

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

5.5 INITIAL CALIBRATION

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

5.5.1 Deliverables

- CLP Form VI-VOA-1,2; VI-SVOA-1,2, or equivalent for SW-846 methods
- Raw data (required for confirmation)

5.5.2 Frequency

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

5.5.3 Criteria

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

Table 5 lists performance criteria for initial calibration.

Table 5. On-Column Standard Concentrations and Performance Criteria for Initial Calibration

CLP **Organic SOW 5/99 OLM04.2**	**SW-486** **Method 8260 (VOA)** **Method 8270 (SVOA)**
10, 20, 50, 100, 200 µg/L VOA	5 levels minimum, lowest near but > MDL
20, 50, 80, 120, 160 µg/L SVOA	SW8270–Mean RF for system performance check compounds (SPCCs) ≥ 0.05
Minimum RRF of ≥ 0.05 except CCCs*	RSD ≤ 40.0% for compounds in Table 4–6 or 30.0% for all other compounds
All compounds, RSD ≤ 30.0%	Linear calibration option: 0.995 or better
	Quadratic calibration option: 0.99 or better

*CCC = column control compounds relative response factor (RRF) of > 0.1

5.5.4 Data Verification

The data verifier shall confirm the presence of required reporting forms. If they are not provided, contact the laboratory and request they be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems and shall be identified in this way on the data verification checklist. Place qualification code C07 on the affected data, if noncorrectable deliverable deficiencies have occurred. Qualify only if the deviation indicates an adverse effect on data quality.

5.5.5 Data Validation

If initial RRF of any compound is < 0.05 in the initial calibration, all samples related to the initial calibration shall be qualified because of reduced instrument sensitivity. Results at or near the instrument detection limit are impacted and are qualified as “R” because of the potential for reporting false negatives. Detected results are qualified as “J.”

If the RRF (CLP) or RF (SW-846) of any compound is < 0.05, qualify detected results with positive mass spectral identification as “J” and nondetected results as “R.”

If the percent relative standard deviation (%RSD) among the calibration points is > 30% or 40% (for compounds listed in Table 6), and the RRF/RF is > 0.05, qualify detected results as “J” and nondetected results as “UJ.” If upon inspection of raw data nondetected results are suspected to be reported falsely, apply professional judgment.

Table 6. Volatile and Semivolatile Target Compounds Exhibiting Poor Response

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

If both the RRF/RF is < 0.05 and %RSD is > 30% or 40% (for compounds listed in Table 6), qualify detected results as "J" and non-detected results as "R."

If the %RSD is > 30% or 40% (for compounds listed in Table 6), this indicates nonlinearity in the calibration curve. Elimination of either the highest or lowest point in the curve may restore the %RSD. Recalculate the %RSD excluding the highest point and then excluding the lowest point.

- If elimination of either point does not restore %RSD < 30% or 40% (for compounds listed in Table 6), qualify detected results as "J" and nondetected results as "UJ" or "R."

- If elimination of the high point restores %RSD < 30% or 40% (for compounds listed in Table 6), qualify detected results as "J" and apply no qualification to nondetected results.

- If elimination of the low point restores %RSD < 30% or 40% (for compounds listed in Table 6), qualify low-level positive results as "J." Use professional judgment to qualify nondetected results.

The laboratory may elect to calculate a linear or quadratic calibration curve. If this method is used, there are two options as follows: Option 1: linear least squares regression r ≥ 0.995; or Option 2: non-linear regression coefficient of determination ≥ 0.99 (6 points shall be used for second order; 7 points shall be used for third order).

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

For Level IV data validation only, conduct raw data confirmation by inspecting for instances of manual integrations of peak areas. Recurring manual integrations on similar peaks within a calibration, manual integrations on peaks with normally good symmetry, and peak splitting manual integrations shall be inspected to determine the necessity for integration or 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, rationale should be provided in the data package for the noncompliance.

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

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

Initial Calibration				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Has the initial calibration been performed within 12 hours of a GC/MS performance check **AND** prior to any sample analysis?				*	*
2. Are all compounds' average RRF ≥ 0.05 and CCC RRF ≥ 0.01?				J	R
3. Are all compounds' %RSD among calibration points < 30% or 40%***? Or does %RSD meet linear/quadratic requirements?				J	UJ
4. Does an elimination of either high or low points restore %RSD < 30% or 40% ***?				J**	UJ/R/NA*
5. Do samples with differing matrices have matching initial calibration matrices?				Refer to step 5.5.5 or the method being reviewed	
6. Have raw data been examined for anomalies? (Level IV validation only)				Refer to step 5.5.5 or the method being reviewed	
7. Have the quantitation ions of 2 compounds been confirmed at the correct ions for quantitation? (Level IV validation only)				Refer to step 5.5.5 or the method being reviewed	
8. Have raw data been inspected for manual integrations? (Level IV validation only)				Refer to step 5.5.5 or the method being reviewed	

*Qualify only if the deviation indicates an adverse effect on data quality.
**Qualify only peaks outside linear portion.
***Poor response compounds

5.6 INITIAL AND CONTINUING CALIBRATION VERIFICATION

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

5.6.1 Deliverables

- CLP Form VII-VOA-1,2; VII-SVOA-1,2, or equivalent for SW-846 methods, for each GC/MS system used
- Raw data (required for confirmation)

5.6.2 Frequency

Calibration is verified for VOA and SVOA initially following calibration typically using a second source reference standard and once per 12-hour period in which samples are analyzed. The continuing calibration standard must be analyzed prior to sample analysis.

5.6.3 Criteria

The Table 7 lists performance criteria for ICV/CCV.

Table 7. ICV/CCV Performance Criteria

CLP **Organic SOW 5/99-OLM04.2**	**SW-846** **Method 8260 (VOA)** **Method 8270 (SVOA)**
50 µg/L	Mid-level standard—run every 12 hours
Minimum RRF of ≥ 0.05, %D < 25% from initial calibration	8260—Mean RF for SPCCs: ≥ 0.3 for chlorobenzene and 1,1,2,2-tetrachloroethane ≥ 0.1 for bromoform, chloromethane, and 1,1-dichloroethane 8270—Mean RF for SPCC: ≥ 0.05 8260 and 8270—%D ≤ 40% for compounds in Table 6 or 25% for all other compounds from initial calibration

5.6.4 Data Verification

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

5.6.5 Data Validation

If the percent difference (%D) exceeds ± 25% or 40% (for compounds listed in Table 6) and the RRF is ≥ 0.05, then qualify detected results as “J” and nondetected results as “UJ.”

If the RRF is < 0.05, then qualify detected results with acceptable mass spectral identification as “J” and use professional judgment when qualifying nondetected results.

If both the RRF is < 0.05 and %D exceeds ± 25% or 40% (for compounds listed in Table 6), then qualify detected results as "J." Professional judgment will be used to determine the effect to nondetect results.

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

Continuing Calibration				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Has the continuing calibration been performed within 12 hours in which samples are analyzed?				*	*
2. Is average RRF of all compounds ≥ 0.05?				J	***
3. Is %D between initial and continuing calibration points < 25% or 40% for all compounds?**				J	UJ
4. Is RRF < 0.05 and %D > 25% or 40%**?				J	***
5. Do samples quantified against the initial calibration use 50 µg/L (VOA) and 80 µg/L (SVOA)?					

*Qualify only if the deviation indicates an adverse effect on data quality.
**Poor response compounds (Table 6).
***Use professional judgment when qualifying nondetected results.

5.7 BLANKS

Blank analyses serve to determine the existence and magnitude of contamination resulting from laboratory or field activities. A preparation blank or method blank (MB) is used to assess the level of contamination introduced to the analytical samples throughout the sample preparation and analysis process. If contamination is found in any blank, all associated data must be carefully evaluated to determine whether or not there is a systemic problem affecting greater than one sample or if the contamination is an isolated occurrence.

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 introduced during field handling, storage, and shipping of samples. A trip blank should be collected and included with all VOA samples collected for analysis.

Additionally, the project team may elect to collect and analyze field and equipment rinseate blanks 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. The equipment rinseate blank provides an indication as to whether or not non-dedicated sampling equipment has been properly decontaminated, and what, if any, carry over may arise between sampled locations. It has been EPA Region 4 data validation policy to evaluate the trip blanks, field blanks, and equipment rinseate blanks as part of the validation process, but not to qualify the data based on these field samples.

5.7.1 Deliverables

- CLP Form I VOA-1,2; VII-SVOA-1,2, and CLP Form IV VOA, SV or equivalent for SW-846 methods, for each method blank

- Raw data (required for confirmation)

5.7.2 Frequency

For CLP (Organic SOW-5/99 OLM04.2), the MB for VOA analysis should be analyzed after the calibration standards and once for every 12-hour time period beginning with the injection of 4-bromofluorobenzene. The MB for VOAs should be analyzed on each GC/MS system used to analyze samples of each matrix type. The IB for VOAs should be analyzed after any samples that have saturated ions from a given compound to check for carryover. For SVOA analysis, the MB should be analyzed once per SDG; each 14-day period during which samples are received; each 20 samples in an SDG; or whenever samples are extracted by the same procedure.

For SW-486 (Method 8260—VOA and 8270—SVOA), the MB should be analyzed for each batch (maximum of 20 samples per batch).

5.7.3 Criteria

Compounds detected in blanks analyzed under CLP must be at levels < reporting limit (RL). Blank performance criteria are not specified for SW-846 methods. For the purposes of data validation, blank contamination shall be evaluated against CLP guidelines.

For volatile analyses, the blank must contain < 2.5 × RL for methylene chloride, < 5 × RL for acetone and 2-butanone, and < RL for all other target compounds.

For semivolatile analyses, the method blank must contain < 5 × RL for phthalate esters and < RL for all other target compounds.

5.7.4 Data Verification

Verify the presence of required reporting forms. If they are not provided, contact the laboratory and request that they be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems. Place qualification code “B07” on the affected data if noncorrectable deliverable deficiencies have occurred; qualify only if the deviation indicates an adverse effect on data quality.

5.7.5 Data Validation

Any compound that is reported in both the blank and sample must be evaluated; however, if the same compound is reported in a sample and more than one blank, the sample shall be evaluated against the blank with the highest concentration of the compound. Sample results must <u>not</u> 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 sample concentration is > RL and > 5 × blank concentration (10 × for common laboratory contaminants, see note below), then no qualification of results is necessary.

If sample concentration is > RL and < 5 × blank concentration (10 × for common laboratory contaminants), then qualify the reported result as "U."

If gross contamination (saturated peaks in blank) is present, then qualify all affected results as "R."

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

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

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

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

Method Blank				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Was the method blank analyzed at the appropriate frequency?				*	*
2. Was the method blank the same matrix as the samples?					
3. Are sample results > RL and > 5×** blank result?					
4. Is sample result > RL and < 5×** blank result?				U	N/A
5. Is sample result < RL and < 5×** blank result?				U	N/A
6. Gross contamination (use professional judgment)				R	N/A
7. Confirm from raw data that compounds reported in the method blank are detected above the RL.					

*Qualify only if the deviation indicates an adverse effect on data quality.
**10 × for common lab contaminants.

5.8 SURROGATE STANDARDS

Surrogate standards are nontarget compounds added to all analytical samples, blanks, and QC samples to assess overall system performance. These standards are added prior to GC/MS purge in water samples analyzed for volatiles, and before extraction in soil samples analyzed for volatiles and soil and water samples analyzed for semivolatiles.

5.8.1 Deliverables

- CLP Form II VOA-1,2; Form II-SVOA-1,2, or equivalent for SW-846 methods, including surrogate recoveries for all samples, blanks, and QC samples

- Raw data (required for confirmation)

5.8.2 Frequency

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

5.8.3 Performance Criteria

Table 8 lists recovery limits for volatile surrogates and Table 9 lists recovery limits for semivolatile surrogates.

Table 8. Volatile Surrogate Recovery Limits

Compound	Water		Soil	
	OLM04.2	SW-846 Method 8260	OLM04.2	SW-846 Method 8260
Toluene-d8	88-110	88-110*	84-138	81-117*
Bromofluorobenzene	86-115	86-115*	59-113	74-121*
1,2-Dichloroethane-d4	76-114	80-120*	70-121	80-120*
Dibromofluoromethane	Not required	86-118*	Not required	80-120*

*For Method 8260, compare surrogate %R to laboratory and established limits. If no laboratory limits are available, these limits may be used.

Table 9. Semivolatile Surrogate Recovery Limits

Compound	Water		Soil	
	OLM04.2	SW-846 Method 8270	OLM04.2	SW-846 Method 8270
Nitrobenzene-d5	35-144	Lab-determined limits**	23-120	Lab-determined limits**
2-Fluorobiphenyl	43-116	Lab-determined limits**	30-115	Lab-determined limits**
Terphenyl-d14	33-141	Lab-determined limits**	18-137	Lab-determined limits**
Phenol-d5	10-110	Lab-determined limits**	24-113	Lab-determined limits**
2-Fluorophenol	21-110	Lab-determined limits**	25-121	Lab-determined limits**
2,4,6-Tribromophenol	10-123	Lab-determined limits**	19-122	Lab-determined limits**
2-Chlorophenol-d14	33-110*	Not required	20-130*	Not required
1,2-Dichlorobenzene-d4	16-110*	Not required	20-130*	Not required

*Advisory limits.
**For Method 8270, compare surrogate %R to laboratory-established limits. If no laboratory limits are available, the CLP limits listed may be used.

5.8.4 Data Verification

Verify the presence of required reporting forms. If they are not provided, contact the laboratory and request that they be provided. If these occurrences cannot be resolved with the analytical laboratory, they are considered noncorrectable problems. Place qualification code “S06” on the affected data if noncorrectable deliverable deficiencies have occurred; qualify only if the deviation indicates an adverse effect on data quality.

5.8.5 Data Validation

Qualify data if either of the following conditions is met:

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

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

Volatile Analysis

- If any surrogate %R exceeds the upper control limit, then qualify detected results as "J" and accept nondetected results.

- If any surrogate %R is between 20% and the lower control limit, then qualify detected results as "J" and nondetected results as "UJ."

- If any surrogate %R < 20%, then qualify detected results as "J" and nondetected results as "R."

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

Semivolatile Analysis

- If the surrogate %R exceeds the upper acceptance limit, then qualify detected results for that fraction as "J" and accept nondetected results.

- If one or more base-neutral or acid surrogate %R is between 10% and the lower control limit, then qualify detected results for that fraction as "J" and nondetected results for that fraction as "UJ."

- If any surrogate %R < 10%, then qualify detected results for that fraction as "J" and nondetected results for that fraction as "R."

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

- If recalculation of the surrogate concentrations or recoveries does 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 the following criteria:

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

Surrogate Standards				Qualification Guidance	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Have surrogate standards been analyzed at the proper frequency?				*	*
2. Have the proper surrogate standards been used?				*	*
3. Are all surrogate standard %R within established criteria?					
Is %R > upper control limit?				J	N/A
Is %R ≥ 10% and < lower control limit?				J	UJ
Is %R < 10%?				J	R

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

5.9 INTERNAL STANDARDS

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

5.9.1 Deliverables

- CLP Form II VOA-1; Form VIII SV-1, or equivalent for SW-846 methods
- Raw data (required for confirmation)

5.9.2 Frequency

Internal standards are added to all analytical samples, blanks, and quality control samples prior to purging for volatile water and soils, and are added prior to extraction of semivolatile and volatile medium level soils.

5.9.3 Criteria

Table 10 provides volatile and semivolatile internal standards.

Table 10. Volatile and Semivolatile Internal Standards

SVOA Internal Standards (CLP & SW-846)	VOA Internal Standards (CLP)	VOA Internal Standards (SW-846)
1,4-Dichlorobenzene-d4	Bromochloromethane	Fluorobenzene
Napththalene-d8	1,4-Difluorobenzene	Chlorobenzene-d5
Acenaphthene-d10	Chlorobenzene-d5	1,4-Dichlorobenzene-d4
Phenanthrene-d10	-	-
Chrysene-d12	-	-
Perylene-d12	-	-

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

5.9.4 Data Verification

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

considered noncorrectable problems. Place qualification code “I07” on the affected data if noncorrectable deliverable deficiencies have occurred; qualify only if the deviation indicates an adverse effect on data quality.

5.9.5 Data Validation

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

If peak area %D < 50%, then qualify detected results as “J” and nondetected results as “UJ.”

If peak area %D > 200%, then qualify detected results as “J” and accept nondetected results.

If a performance drop is indicated by extremely low area counts (< 20%), then qualify detected results as “J” or “R” if the performance drop has significantly affected sample results and nondetected results as “R.”

If Internal Standard retention times vary by more than ± 10 seconds (between the sample internal standard and calibration internal standard), conduct confirmation of raw data for Level IV data validation only by examining the chromatographic profile for that sample to determine if any false positives or negatives exist. Qualify false positive results or false negative detection limits with professional judgment as appropriate.

Internal Standards				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Have the proper internal standards been used?				*	*
2. Are peak areas %D between -50% and +100% of the continuing calibration internal standard peak areas?					
If %D < 50%				J	UJ/R
If %D > 200%				J	N/A
Extremely low area counts in more than one area				J/R	R
3. Does the internal standard retention time vary more than 10 seconds from continuing calibration?				J/R**	R**

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

**Qualify as appropriate.

5.10 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

The purpose of the matrix spike/matrix spike duplicate (MS/MSD) differs from the CLP 5/99 SOW to the SW-846 methods. For CLP, the MS/MSD are analyzed to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. For SW-846, the MS/MSD are analyzed to determine the accuracy of the method. If recovery criteria are not satisfied for the SW-846 methods, there is difficulty in assessing whether the cause was the method or matrix-related interferences. To address this issue, LCS/LCS duplicate (LCSD) also are analyzed to verify whether the methods results themselves are satisfactory. If only the MS/MSD are affected, a matrix effect is likely.

NOTE: For a MS that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available

data, including site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and laboratory data for other parameters (e.g., total suspended solids, total dissolved solids, total organic carbon, alkalinity or buffering capacity, reactive sulfide, anions) in determining similarity. The reviewer also should use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the data package. The reviewer may determine that only some of the samples in the data package are similar to the MS sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the MS and, thus, that only the field sample used to prepare the MS sample should be qualified.

5.10.1 Deliverables

- CLP Form II VOA-1,2, SVOA-1,2, or equivalent for SW-846 methods
- Raw data (required for confirmation)

5.10.2 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.

5.10.3 Criteria

Tables 11 and 12 list CLP performance criteria for MS/MSD.

Table 11. Performance Criteria for VOA MS/MSD

VOA Compound	%R Water	RPD Water	%R Soil	RPD Soil
1,1-Dichloroethene	61-145	14	59-172	22
Trichloroethene	71-120	14	62-137	24
Benzene	76-127	11	66-142	21
Toluene	76-125	13	59-139	21
Chlorobenzene	75-130	13	60-133	21

Table 12. Performance Criteria for SVOA MS/MSD

SVOA Compound	%R Water	RPD Water	%R Soil	RPD Soil
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
4-Chloro-3-methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10-80	50	11-114	50
2,4-Dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

For SW-846 methods, the MS/MSD %R should fall within laboratory-determined limits. If MS/MSD results fall outside the laboratory-determined limits, a QC Check Standard or LCS must be analyzed and fall within those ranges. The CLP criteria can be used as a guide to evaluate laboratory performance if limits have not been established or are not provided.

5.10.4 Data Verification

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

5.10.5 Data Validation

A determination shall be made concerning what extent that noncompliant MS/MSD data has on other sample data in regard to the MS/MSD sample itself as well as specific compounds in samples associated with the MS/MSD. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, then qualification shall be limited to that sample alone; however, it may be determined that the laboratory is having a systematic problem in the analysis of one or more compounds, which affects all associated samples. The MS/MSD also shall be reviewed to determine if there is an overall bias to the sample or base neutral acid fraction, such as the majority of compounds with either a high or low recovery. MS/MSD data alone shall not be used exclusively to qualify data, but in conjunction with other supporting QC data. Professional judgment shall be used to determine the need for qualification of reported compounds.

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

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

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

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

- If poor spike recovery occurs in a sample whose concentration is > 4 × the spiked amount, no qualification is warranted.

- If MS %R > upper control limit, qualify detected analytes as "J" estimated. Nondetects do not require qualification.

- If MS %R > 10% and < lower control limit, qualify detected analytes as "J" estimated and nondetects as "UJ."

- If MS %R < 10%, qualify detected analytes as "J" estimated and nondetects as "R" rejected.

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

- If the relative percent difference (RPD) for water/liquid MS/MSD is > 30%, qualify associated detections as "J" and nondetects as "UJ."

- If the RPD for soil/solid matrices is > 40%, qualify associated detections as "J" and nondetects as "UJ."

Matrix Spike/Matrix Spike Duplicate				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Was the MS/MSD analyzed at the appropriate frequency?				*	*
2. Are all MS/MSD compounds' %R within control criteria?				**	**
3. Are all MS/MSD RPD within control criteria?				**	**

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

5.11 DUPLICATES

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

5.11.1 Deliverables

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

5.11.2 Frequency

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

5.11.3 Criteria

- Samples identified as field blanks must not be analyzed as laboratory duplicate.

- For sample concentrations > 5 × RL, the laboratory duplicate precision for aqueous samples as measured by RPD must be within ± 25% for both VOA and SVOA analyses (lab duplicates and field duplicates). For solid matrices the RPD must be within ± 25% (lab duplicate) or ± 35% (field

duplicates) for both VOA and SVOA analyses. If the sample results are < 5 × RL, RPD does not apply. Instead, the absolute difference between sample and duplicate must be < 5 × RL.

5.11.4 Data Verification

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

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

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

5.11.5 Data Validation

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

Laboratory and field duplicate qualification is provided in Table 13.

Table 13. Laboratory and Field Duplicate Qualification

Duplicate Type	Matrix	RPD	Sample Results	Qualification Instructions
Laboratory Duplicate	Aqueous	>25%	Sample and dup > 5 × RL	Qualify results > RL "J" Qualify nondetects "UJ"
	Solid	>25%		
	Aqueous	> 25%	Sample and dup < 5 × RL	Absolute difference > RL "J" Absolute difference < RL no action
	Solid	>25%		
Field Duplicate	Aqueous	>25%	Sample and dup > 5 × RL	Qualify results > RL "J" Qualify nondetects "UJ"
	Solid	>35%		
	Aqueous	>25%	Sample and dup < 5 × RL	Absolute difference > RL "J" Absolute difference < RL no action
	Solid	>35%		

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

Duplicate				Qualification Guidance	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have the duplicate results been included in the data package?				----	----
2. Was the duplicate analyzed at the appropriate frequency? *				----	----
3. Were the duplicate RPDs within control criteria? **				J	UJ

*Qualify only if the deviation indicates an adverse effect on data quality.
**Qualify only if other QC data in the SDG is outside established criteria.

5.12 LABORATORY CONTROL SAMPLE

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

5.12.1 Deliverables

- Report summary of all analytes in the LCS
- Raw data (required for confirmation)

5.12.2 Frequency

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

5.12.3 Criteria

The LCS must be analyzed and must fall within limits specified by the determinative method.

The LCS is not required for the CLP 5/99 SOW, but is required for the SW-846 methods 8260 and 8270. Four replicates of the LCS are extracted and analyzed as an initial, one-time demonstration of ability to generate acceptable accuracy and precision. The LCS procedure may need to be repeated if changes in instrumentation or methodology occur. A LCS must also be analyzed if MS/MSD results fall outside laboratory-determined limits.

It is recommended that this standard be the same matrix as the analytical samples, and for SVOA analysis 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 addition of a LCS concentrate into the appropriate clean matrix, extracted and analyzed (analyzed only in the case of volatile purge and trap).

5.12.4 Data Verification

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

5.12.5 Data Validation

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

- If all LCS compounds were within laboratory determined limits, then accept all detected and nondetected results.

- If the LCS %R for an analyte is > the upper acceptance limit, detected target compounds may be qualified as "J." Nondetected target compounds should not be qualified.

- If the LCS %R for an analyte is < the lower acceptance limit, qualify detected target compounds as "J" and nondetects estimated as "UJ" or rejected as "R" (use professional judgment).

- If an LCSD is included with the analyses, and the calculated %RPD between the LCS and LCSD results exceeds laboratory limits, qualify associated target analytes "J" or "UJ" as appropriate.

Professional judgment should be used to qualify data for compounds that are included in the LCS. Professional judgment to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in the performance of the LCS compound to the non-LCS compound. Additionally, the following specific guidance is provided to determine qualifications when more than one LCS compound is found to be out of control:

- If one LCS compound but fewer than 50% of the LCS compounds analyzed were outside of the laboratory determined limits and the %R > upper control limit, then qualify associated detected results as "J" and accept associated nondetects..

- If one LCS compound but fewer than 50% of the LCS compounds analyzed were outside of the laboratory determined limits and the %R > 10% but < lower control limit, then qualify associated detected results as "J" and associated nondetects as "R."

- If more than 50% of the LCS compounds reported were outside of the laboratory determined limits, the reviewer should use professional judgment to determine the best approach to qualifying the associated results as this could be an indication of a systematic problem.

Laboratory Control Sample (SW-846 Methods Only)				**Qualification Guidance**	
Validation Step	Yes	No	N/A	Detects	Nondetects
1. Was the LCS analyzed at the proper frequency?				J	UJ
2. Was the LCS prepared and analyzed for SVOA compounds?				*	*
3. Were the %R and RPD (if a LCSD was analyzed) of the reported compounds within acceptance criteria?				J	UJ/R

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

5.13 REPORTING LIMITS/SAMPLE QUANTITATION LIMITS

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

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

5.13.1 Deliverables

- CLP Form I VOA-1,2, SV-1,2, or equivalent for SW-846 analytical methods for all samples

5.13.2 Frequency

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

5.13.3 Data Verification

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

5.13.4 Data Validation

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

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

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

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, aliquot, if necessary.

No additional validation qualifiers are necessary for results detected below the SQL unless directed in other sections of this plan.

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

5.14 TARGET COMPOUND IDENTIFICATION

5.14.1 Deliverables

- CLP Form I VOA-1,2, SV-1,2, or equivalent for SW-846 analytical methods
- Raw data (required for confirmation)

5.14.2 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 greater than 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.

5.14.3 Data Validation

The presence/absence and concentration of detected compounds in the samples are reviewed to determine whether or not the correct quantitation ions have been used for proper quantification of the compounds. If incorrect ions have been shown, rationale should be provided in the data package for the noncompliance. If no rationale has been provided, evaluation of the effect on quantitation of detected target compounds shall be made. If detected target compounds quantified against the incorrect ion are significantly affected, the affected compounds may be qualified as “R.”

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 had an effect on a compound, such as reporting of false positives or artificially elevating compound levels, affected data may be qualified as “R.”

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

5.15 MANUAL RECALCULATION OF ANALYTICAL RESULTS

The accuracy and consistency of sample result calculation by the laboratory can be addressed using two different techniques. The application of each strategy depends on the laboratory's ability to minimize transcription during reporting, and how familiar the project is with the performance of the laboratory. If sample results are produced primarily through software processing and minimal transcription is performed in the laboratory, the data system(s) can be evaluated during an audit or surveillance by performing two different tests on the software. First, supply the data system a consistent set of input designed to provide a consistent set of output. Next, supply the data system a set of nonconforming data to test the error detection routines. An additional evaluation of the laboratory's software configuration control and security is also necessary. Through this technique, a high level of confidence can be gained in

the laboratory's reporting techniques and will result in a minimal need for manual recalculation of sample results.

If the laboratory has a high rate of manual transcription in generation of sample results, the project may choose to manually recalculate sample results at a determined frequency. If sample results cannot be reproduced through manual calculation, contacting the laboratory may be necessary to resolve the problem. Data may be qualified "R" as a last resort, if no actions can reproduce reported values.

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

5.16 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.

5.16.1 Deliverables

- CLP Form I VOA, SV, or equivalent for SW-846 analytical methods for all samples
- Raw data (required for confirmation)

5.16.2 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.

5.16.3 Data Verification

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

5.16.4 Data Validation

Check raw data against TIC report ensuring that all TIC peaks are accounted on CLP Form I.

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/qualification of TICs:

- Qualify all TICs as "NJ," presumptively identified, at estimated concentration.
- Mass spectra for all samples with raw data and blanks shall be examined for TICs.
- All ions > 10% relative intensity in the reference spectrum should be in the sample spectrum.
- Relative intensity of the major ions should agree within $\pm$ 20% between sample and reference spectra.

- Molecular ions present in the reference spectrum should be present in the sample spectrum.

- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or co-elution of additional TIC or target compounds.

- If the identification is uncertain or there are extenuating factors affecting compound identification, 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, qualify as "R."

- 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 library search does not yield conclusive evidence from items stated above, change the identification of the TIC to "unknown." 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. Qualify these compounds as "R" if reported as TICs.

- If a TIC is reported in one or all samples but not in the blank, check if the compound is a common laboratory artifact in the sample and inspect the blank for peaks that are < 10% of the internal standard area but are present in the blank chromatogram at a similar retention time. Qualify compounds as "R."

- Compounds reported as a TIC in one fraction shall be qualified as "R" in that 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 non-target compound, which is a common artifact or laboratory contaminant, is detected in a sample, a thorough check of blank chromatograms may require looking for peaks that are < 10% of the internal standard area but present in the blanks chromatogram at similar relative retention time.

- If target compounds are identified by nontarget library searches, 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

- CO_2 (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 (flurotrichloromethane or Freon 113)

- Phthalates at levels < 100 µg/L (waters) or 4,000 µg/Kg (soils)

Solvent Preservatives and By-Products

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

Aldol Reaction Products of Acetone

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

6. RECORDS

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

- Data Verification Checklist (for Level II, III, and IV validation only)
- Data Validation Report (for Level III and Level IV validation only)
- Copies of qualified or unqualified results reports (if applicable)

7. REFERENCES

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

Contract Laboratory Program National Functional Guidelines for Organic Data Review, EPA-540/R-00/008, U.S. Environmental Protection Agency, Washington, DC January 2010.

Contract Laboratory Program Statement of Work for Organic Analysis, Multi-media, Multi-Concentration, EPA-OLM04.2, May 1999, U.S. Environmental Protection Agency, Washington, DC, May 1999.

Guidance on Systematic Planning Using the Data Quality Objective Process, EPA/240/B-06/001, U.S. Environmental Protection Agency, Washington, DC, February 2006.

Paducah Gaseous Diffusion Plant Programmatic Quality Assurance Project Plan, DOE/LX/07-1269&D2/R2, U.S. Department of Energy, Paducah, KY.

Quality Assured Data, CP3-ES-5003, Fluor Federal Services, Inc., Paducah Deactivation Project.

Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Revisions through Update III, U.S. Environmental Protection Agency, Washington, DC, March 2009.

APPENDIX A

DATA VALIDATION QUALIFIERS AND QUALIFICATION CODES

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DATA VALIDATION QUALIFIERS AND QUALIFICATION CODES

Data Validation Qualifiers

U Analyte compound or nuclide considered not detected above the reported detection limit.
J Analyte compound or nuclide identified; the associated numerical value is approximated.
NJ Analyte compound or nuclide presumptively present at an estimated quantity.
UJ Analyte compound or nuclide not detected above the reported detection limit, and the reported detection limit is approximated due to quality deficiency.
R Result is not usable for its intended purpose.
= "Equals" sign, indicates that no qualifier is necessary.

Data Validation Qualification Codes

Blanks
B01 Sample concentration was < the RL, and < 5 × the blank concentration (10 × for common contaminants).
B02 Sample concentration was > 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 RRF was < 0.05
C02 Initial calibration %RSD was exceeded
C03 Initial calibration sequence was not follows as appropriate
C04 Continuing calibration RRF was < 0.05
C05 Continuing calibration %D was exceeded
C06 Calibration or performance check was not performed at the appropriate frequency
C07 Calibration data not reported
C08 Calibration not performed
C09 Chemical resolution criteria were not satisfied
C10 Calibration standard matrix not the same as sample matrix
C11 Compounds quantitated against inappropriate standard or standard concentration level
C12 Compound quantitated against inappropriate ion
C13 Calibration factor RSD criteria were not satisfied
C14 Retention time of compound outside window
C15 Initial calibration % R was below lower acceptance limit
C16 Initial calibration % R was above upper acceptance limit
C17 Initial calibration curve fit was < 0.995
C18 Inappropriate standard concentrations

C19 Continuing calibration R was below the lower acceptance limit
C20 Continuing calibration %R was above the upper acceptance limit
C21 CRI %R was below the lower acceptance limit
C22 CRI %R was above the upper acceptance limit
C24 Standard curve was established with fewer than the appropriate number of standards
C27 Calibration verification efficiency outside control criteria
C28 Calibration verification background outside control criteria
C29 Calibration verification energy outside control criteria
C30 Calibration verification peak resolution outside control criteria
C31 Chromatogram does not show adequate gain setting
C32 Other (describe in comments)

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

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

Interference Check Samples (ICS)
F01 ICS recovery below lower control limit or advisory limit
F02 ICS recovery above upper control limit or advisory limit

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

Holding Times/Preservation
H01 Extraction holding times were exceeded
H02 Extraction holding times were grossly exceeded
H03 Analysis holding times were exceeded
H04 Analysis holding times were grossly exceeded
H05 Samples were not preserved properly
H06 Sample preservation cannot be confirmed
H07 Sample temperature exceeded criteria prior to preparation
H08 Other (describe in comments)

Internal Standards
I01 Area count was above upper control limits
I02 Area count was below lower control limits
I03 Extremely low area counts or performance was exhibited by a major drop off
I04 Internal standard retention time varied by more than 30 seconds
I05 Inappropriate internal standard used
I06 Inappropriate internal standard concentration(s) used

I07 Internal standard data not reported
I08 Other (describe in comments)

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

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

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

Quantitation
Q01 Peak misidentified
Q02 Target analyte affected by interfering peak
Q03 Qualitative criteria were not satisfied
Q04 Cross contamination occurred
Q07 Analysis occurred outside 12 hour GC/MS window
Q09 TIC result was not above 10× the level found in the blank
Q10 TIC reported as detect in another fraction
Q11 Common artifact reported as a TIC
Q12 No raw data were provided to confirm quantitation
Q13 MDA > RL
Q14 Inappropriate aliquot sizes were used
Q15 Sample result < MDA
Q16 Sample result < 2σ uncertainty
Q17 Negative result
Q18 Compounds were not adequately resolved
Q19 Sample geometry different from calibration geometry
Q20 Sample weight greater than greatest weight on mass attenuation curve
Q21 Isotopes of same radionuclide do not show equilibrium

Q22 Peak not within appropriate energy range
Q23 Counting uncertainty ≥ 80% of sample result
Q24 Raw data anomaly
Q25 Other (describe in comments)
Q26 RT outside calculated RT window
Q28 Neither RL or the SQL are reported for a nondetect result
Q29 SQL > RL
Q30 Compound detected at < SQL and not qualified "J"
Q31 Presence of high molecular weight contaminants impacted sample quantitation

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

Instrument Tuning
T01 Mass calibration ion misassignment
T02 Mass calibration was not performed every 12 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 GPC calibration not checked at required frequency
U03 GPC calibration criteria not met
U04 GPC blank not analyzed after GPC calibration
U05 GPC blank greater than half the RL for target compound

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

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

Radiochemical Yield

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

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APPENDIX B

QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

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QUALIFICATION TABLES FOR MULTIPLE QUALITY DEFICIENCIES

Guidance for Data Qualification Due to Multiple Quality Deficiencies

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

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

Data Quality Indicator	Effect on Sample Data
GC/MS tuning	Compound identification
Initial calibration	Identification and quantitation
Continuing calibration	Quantitation
Surrogate standards	Positive or negative bias
Internal standards	Positive or negative bias
Method blank	Positive bias
LCS/LCS duplicate	Method bias and precision
MS/MS duplicate	Positive or negative bias and precision
QC check standard	Positive or negative bias

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

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APPENDIX C

RULES, CALCULATIONS, AND EQUATIONS

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RULES, CALCULATIONS, AND EQUATIONS

Rounding Rules

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

Calculations/Equations

C.1 Calculation for 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 %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

$$RPD = \frac{|R_1 - R_2|}{\bar{R}_1, R_2} x100$$

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

C.7 Sample Quantitation Limit

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

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

C.8 Waters

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

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

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

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

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