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CP2-ES-0026/FR1A

Wet Chemistry and Miscellaneous Analyses Data Verification and Validation Paducah Gaseous Diffusion Plant, Paducah, Kentucky

FOUR RIVERS NUCLEAR PARTNERSHIP, LLC

This document is approved for public release per review by:

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

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APPROVALS

Wet Chemistry and Miscellaneous Analyses
Data Verification and Validation
Paducah Gaseous Diffusion Plant,
Paducah, Kentucky

CP2-ES-0026/FR1A

Lisa Crabtree
Environmental Monitoring Manager

12/12/17
Date

Curt Walker
Environmental Services Project Director

12/13/17
Date

DOE Approval Letter: N/A

Date: N/A

Nuclear Safety Documentation: N/A

Non-intent changes per CDL- USQ not required

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REVISION LOG

REVISION NUMBER	DATE	DESCRIPTION OF CHANGES	PAGES AFFECTED
FR0	**10/20/17**	**Bluesheet**	**ALL**
FR1	**12/13/17**	**Non-Intent Changes for Bluesheet Incorporation**	**ALL**
FR1	**7/6/2021**	In accordance with the Corrective Action Plan for CAPA CA-003116, Action Item AI-0004735 and CAPA CA-003086, Action Item AI-0004709, the periodic review date for this procedure has been Extended to December 13, 2022.	**1**
FR1A	**12/13/2022**	**Periodic Review has been completed with no changes identified in procedure technical content. Nonintent changes have been incorporated per CP3-NS-2001. Date for review cycle has been reset**	**ALL**

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CONTENTS

TABLES

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ACRONYMS

CCV	continuing calibration verification
CLP	Contract Laboratory Program
COC	chain of custody
DQO	data quality objective
EDD	electronic data deliverable
EPA	U.S. Environmental Protection Agency
ICV	initial calibration verification
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MS	matrix spike
MSD	matrix spike duplicate
QAPP	quality assurance project plan
QC	quality control
RL	reporting limit
RPD	relative percent difference
SDG	sample delivery group
SMO	Sample Management Office
SOW	statement of work
TDS	total dissolved solids
TOC	total organic carbon
TSS	total suspended solids
%R	percent recovery

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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.

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

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

CONTINUING CALIBRATION VERIFICATION—A standard solution analyzed at a specified frequency during an analytical run to assure 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 OBJECTIVES—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 EPA 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.

LABORATORY CONTROL SAMPLE—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—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.

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.

QUALITY-INDICATOR SAMPLE—Quality-indicator samples are those samples made ready in the laboratory that provide direct or indirect evaluation of the status of the analytical system and resulting data quality. Collectively, quality indicator samples are the laboratory control sample, laboratory duplicate, matrix spike, and method blank.

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

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

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

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

VALIDATION 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.

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1. INTRODUCTION

1.1 PURPOSE, SCOPE, AND APPLICATION

1.1.1 Purpose

This plan defines the minimum requirements, responsibilities, and methodology for the wet chemistry and miscellaneous analyses data verification and validation processes for evaluating analytical data generated using industry standard measurement techniques.

This plan is applicable to routine analyses for common wet chemistry parameters primarily in aqueous and soil/sediment matrices. Examples include traditional water quality parameters (sulfate, chloride, nitrate, etc.).

This plan also applies to the verification and validation of data obtained for non-routine miscellaneous analyses. Examples include determination of waste characteristics and other non-routine analyses (flashpoint, coliform, etc.).

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 data validation requirements is recommended. This plan shall be used as a baseline to create project-specific reports needed to perform wet chemistry and miscellaneous data verification and validation.

1.1.2 Scope and Application

This plan applies to wet chemistry and miscellaneous 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 wet chemistry and miscellaneous 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., U.S. Environmental Protection Agency (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 Data 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)				
Contract Laboratory Program (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
(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

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

Report Elements to be Reviewed*	Level I	Level II	Level III	Level IV
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/miscellaneous methods with no true calibration information will not have calibration forms included in the data package.

The requirements of the Level I and Level II review and validation effort will be referred to as "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 that 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 a 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 5.0 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 wet chemistry and miscellaneous 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 (if required), instrument performance (if required), batch quality control samples (e.g., laboratory control sample), the identification and quantitation of target analytes, performance standards (e.g., surrogates, internal standards) and the effect quality control (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 data 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 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 requests only.)

The validation SOW will include as attachments full copies of the analytical 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.

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 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 data verifier's or data 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 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 validation strategy based on inputs identified through the data quality objective (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 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 one of the following conditions is 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: Data 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	NA
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 re-extraction 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 routine analyses generally determined by wet chemistry and miscellaneous methods. In all cases, the data verifier or data validator shall always follow the most current methodology guidance for sample holding time, temperature, and preservation requirements.

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. Wet chemistry and miscellaneous parameters preservatives and holding times are provided in Table 2.

Table 2. Wet Chemistry and Miscellaneous Parameters Preservatives and Holding Times

Parameters	Matrix	Preservatives	Holding Times
Acidity	Liquid	0–6°C	14 days
Alkalinity	Liquid	0–6°C	14 days
Biochemical Oxygen Demand (BOD)	Liquid	0–6°C	48 hours
Bromide	Liquid/Solid	0–6°C	28 days
Carbonaceous Oxygen Demand (CBOD)	Liquid	0–6°C	48 hours
Chemical Oxygen Demand	Liquid	0–6°C, H_2SO_4 to pH < 2	28 days
Chloride	Liquid/Solid	0–6°C	28 days
Color	Liquid	0–6°C	48 hours
Conductivity	Liquid	0–6°C	28 days
Corrosivity by pH	Liquid/Solid	None	Immediate
Dissolved Oxygen	Liquid	Zero headspace	Immediate
Flashpoint	Liquid/Solid	None	None
Fluoride	Liquid/Solid	0–6°C	28 days
Hardness	Liquid	HNO_3 or H_2SO_4 to pH< 2	6 months
Heating Value	Solid	None	None
Hexavalent chromium	Liquid	0–6°C	24 hours
Hexavalent chromium	Liquid	0–6°C, $(NH_4)^2SO_4$, pH=9.3-9.7	28 days
Hexavalent chromium	Solid	0–6°C	7 days for extraction, 30 days for analysis
Iodide	Liquid	0–6°C	
Nitrogen—Ammonia	Liquid/Solid	0–6°C, H_2SO_4 to pH < 2	28 days
Nitrate	Liquid/Solid	0–6°C	48 hours
Nitrite	Liquid/Solid	0–6°C	48 hours
Nitrate/Nitrite	Liquid/Solid	0–6°C, H_2SO_4 to pH < 2	28 days

Table 2. Wet Chemistry and Miscellaneous Parameters Preservatives and Holding Times (Continued)

Parameters	Matrix	Preservatives	Holding Times
Nitrogen—Total Kjeldahl	Liquid/Solid	0–6°C, H_2SO_4 to pH < 2	28 days
Odor	Liquid	0–6°C, Zero headspace	Immediate
Oil and Grease	Liquid	0–6°C, HCl or H_2SO_4 to pH < 2	28 days
Orthophosphate	Liquid/Solid	Filter immediately, 0–6°C	48 hours
Paint Filter Liquids Test	Liquid/Solid	None	None
Percent (%) Moisture	Liquid/Solid	0–6°C	None
Phenols, Total	Liquid/Solid	0–6°C, H_2SO_4 to pH < 2	28 days
pH	Liquid/Solid	None	Immediate
Phosphorus, Total	Liquid/Solid	0–6°C, H_2SO_4 to pH < 2	28 days
Residual Chlorine, Total	Liquid	0–6°C	Immediate
Residue, Filterable (TDS)	Liquid	0–6°C	7 days
Residue, Non-Filterable (TSS)	Liquid	0–6°C	7 days
Residue, Total	Liquid	0–6°C	7 days
Residue, Volatile and Fixed (% Ash)	Liquid/Solid	0–6°C	7 days
Residue, Settleable	Liquid	0–6°C	48 hours
Specific Gravity	Liquid	0–6°C	7 days
Sulfate	Liquid/Solid	0–6°C	28 days
Sulfide	Liquid/Solid	0–6°C, add ZnAc & NaOH to pH > 9	7 days
Sulfide, Reactive Releasable	Liquid	Zero headspace	7 days
Sulfide, Reactive Releasable	Solid	Zero headspace	28 days
Sulfite	Liquid	EDTA	Immediate
Total Organic Carbon	Liquid/Solid	0–6°C, HCl or H_2SO_4 to pH < 2	28 days
Total Organic Halides	Liquid/Solid	0–6°C, H_2SO_4 to pH < 2	28 days
Total Petroleum Hydrocarbons	Liquid	0–6°C, H_2SO_4 to pH < 2	28 days
Turbidity	Liquid	0–6°C	48 hours
Uranium by TIMS (Transmission Impairment Measurement Set)	Liquid	0–6°C, HCl or HNO_3 to pH < 2	6 months
Uranium by TIMS	Solid	0–6°C	6 months

*Only used in the presence of residual chlorine.

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 < 2, qualify detected results "J" and nondetected results "UJ."

- If the holding time is exceeded by a factor > 2, qualify affected sample results > method detection limit with a "J" qualifier as estimated quantities and nondetected results "R" rejected due to gross holding time exceedance.

5.3.4.2 Temperature

Review laboratory receiving records to determine if samples were received at the appropriate temperature. If samples have exceeded temperature requirements, the data validator must evaluate the effect on reported results. Depending on the magnitude of the temperature increase, results may or may not be adversely impacted.

If prescribed sample receipt temperatures are exceeded (see Table 2), qualify detected analytes "J" and nondetects "UJ."

If the temperature of samples grossly exceeds the limits prescribed in Table 2 (i.e., > 10°C), the data validator must evaluate the integrity of the reported concentrations. Consultation with the analytical method, other industry standard technical resources, and/or subject matter experts is advised if the temperature requirements are grossly exceeded to determine if sample/analyte degradation has occurred. Data may be qualified "R" if the data validator determines the effect of temperature exceedance has had a significant effect on the accuracy of reported sample results. Justification for "R" qualifiers must be provided in the data validation report.

5.3.4.3 Preservation

If samples have not been preserved properly in the field or have been stored improperly, and there are no established unpreserved holding times, qualify those sample results > RL "J" as estimated quantities and results < RL "R" as rejected values.

If improper storage also results in a loss of proper sample custody or increased sample temperatures, additional qualification may be required. Data validators will evaluate such instances on a case-by-case basis. If a loss of custody or elevated sample temperature(s) coincides with improper storage, qualify affected sample results in accordance with this plan.

Holding Times and Sample Preservation				Qualification Guidance	
Validation Step	Yes	No	NA	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

*Data may be qualified "R" if the reviewer determines the effect of improper preservation has had a significant effect on the accuracy of reported sample results.

5.4 CALIBRATION

Instrument calibration or standardization is performed to ensure the instrument/analytical method is capable of producing quantitative data. Initial calibration/reagent standardization demonstrates that the instrument/method is capable of acceptable performance at the beginning of the analytical run and of producing a linear calibration curve (if applicable for the method used). Initial and continuing calibration verifications demonstrate the method/instrument remains in control throughout sample analysis.

The following subsections present the most common requirements for calibration information related to wet chemistry/miscellaneous analysis; 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 wet chemistry and/or miscellaneous data.

5.4.1 Deliverables

Specific deliverables will depend on the method and instrumentation used for analysis. Deliverables listed below will not be applicable to all wet chemistry and/or miscellaneous methods (e.g., TSS, TDS). For methods where instrument calibration or reagent standardization is not employed to verify method accuracy, independent standards will be employed to provide a measure of method performance (e.g., laboratory control sample and/or matrix spike).

- Calibration Curve (where applicable)
- Reagent Standardization (where applicable)
- Initial Calibration Verification (ICV)
- Continuing Calibration Verification (CCV)
- Analysis Results
- Standard Preparation Log
- Analytical Run Log
- Raw Data (required for confirmation)

5.4.2 Frequency

Depending on the method, initial calibration or reagent standardization must be performed and shown to have an acceptable linearity or recovery before any samples are analyzed.

An ICV may be analyzed in accordance with sample methodology. Typically, an ICV is analyzed immediately following a successful instrument calibration/standardization.

A CCV may be analyzed in accordance with sample methodology. Typically, a CCV is analyzed prior to and following each group of 10 samples or following the last sample in a group—whichever is less.

5.4.3 Criteria

5.4.3.1 Initial calibration

- At a minimum, initial calibration for instrumental methods will consist of a blank and three to five calibration standards bracketing the expected sample concentration(s).

- Typically, an initial calibration is generated daily for instrumental and most meter-type methods (e.g., spectrophotometric, colorimetric, turbidimetric, and ion chromatography) or each time the instrument is set up for analysis, whichever is more frequent.

- Certain analytical methods (such as those utilizing a UV-Vis instrument) allow for the generation of an initial calibration that is stored in the instrument and recalled when needed. If a method allows an initial calibration to be stored and recalled, the calibration must be verified with either an ICV sample or a CCV sample prior to using the instrument.

- The correlation coefficient for a linear calibration curve must be ≥ 0.995.

- For gravimetric methods (e.g., TSS, TDS, etc.), evidence of balance calibration must be provided with the laboratory deliverable to demonstrate proper calibration prior to measurement of sample weights.

- For titrimetric methods (e.g., alkalinity), documentation of titrant standardization must be provided as part of the laboratory deliverable to demonstrate the integrity of the titrant prior to analysis.

- If a pH meter is employed, the meter shall be calibrated with the two pH buffer solutions that bracket sample pH range.

- For nonroutine methods where calibration/standardization is not applicable, an independent check standard (initial calibration verification) will be employed prior to sample analysis to demonstrate the proper functioning of the method prior to sample analysis.

5.4.3.2 Initial calibration verification

For all routine wet chemistry and/or miscellaneous methods employing a calibration, an ICV will be measured prior to the analysis of any project samples. The ICV will be prepared from a source other than that used to prepare calibration standards to demonstrate the method is acquiring accurate data.

The percent recovery (%R) for the ICV will be within limits established by the laboratory or the analytical method as defined by the laboratory SOW. In the absence of previously established limits, the %R for ICVs will be within 90–110%.

5.4.3.3 Continuing calibration verification

For all instrumental and most meter-type methods, a CCV will be analyzed prior to the analysis of any project samples and following each group of 10 samples or at the end of the sample group—whichever is more frequent. The CCV may be prepared from the same source as calibration standards. Typically, the CCV is prepared at the mid-point of the calibration curve to monitor instrument drift during analysis; however, sample analysis methodology will dictate the CCV levels that are acceptable.

The %R for the CCV analysis will be within limits established by the laboratory, the analytical method as defined by the laboratory SOW, or in the requirements identified in a project or program-specific QAPP. In the absence of previously established limits, the %R for CCVs will be within 90–110%.

5.4.4 Data Verification

The data verifier shall verify that appropriate documentation of the initial calibration and the ICV/CCV(s) have been provided in the data package. If any of the following occur, the data verifier shall contact the laboratory immediately to obtain the missing information:

- Evidence of initial calibration, if required, is not included in the laboratory deliverable;
- Frequency of calibration based on the methodology employed has not been satisfied; and/or
- Required numbers of calibration standards or required standard concentrations based on the methodology were not used.

Upon receipt, the information will be placed in the data package for delivery to the data validator.

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. 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.

5.4.5 Data Validation

If an instrument calibration is required, and it was not performed in accordance with the sample methodology, qualify sample results "R" rejected.

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

If the calibration curve does not bracket sample concentrations, determine if a linear range standard has been analyzed demonstrating that the upper linear concentration range of the instrument is capable of quantifying the analyte of interest. If no such standard has been analyzed, the data validator will review raw data and apply professional judgment to determine the effect on positive sample data. Nondetect results are unaffected by this condition. The following are provided as general guidance:

- If instrument responses exceed the calibration range by < 10% but show well resolved peaks (absent chart re-scaling), no qualification of results over the calibration range is required.

- If instrument responses exceed the upper calibration standard by 10–20%, qualify the sample results as "J" estimated.

- If instrument responses grossly exceed the calibration range or saturate the instrument detector, qualify the results "R" rejected.

- If the correlation coefficient for the linear calibration curve is < 0.995, qualify results > RL "J," and results < RL "UJ."

- If the %R for the ICV or CCV is outside control limits, the following actions will be applied to qualify project data:

— If %R = 111–125%, qualify positive results as estimated "J." Nondetect results are acceptable.

— If %R = 75–89%, qualify positive results as estimated "J" and nondetect results as estimated "UJ."

— If %R > 125%, qualify positive results as rejected, "R," nondetect results are acceptable.

— If %R < 75%, qualify all results (detects and nondetects) as rejected, "R."

Calibration				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. If required, was the instrument calibrated at the appropriate frequency?				*	*
2. Was the minimum number of standards used in calibrating the instrument?				*	*
3. Was the regression ≥ 0.995?				J	UJ
4. Were continuing calibration recoveries within control limits? **				J	UJ/R
Is %R > upper control limit?				J	NA
Is %R < lower control limit?				J	UJ

* Qualify only if the deviation indicates an adverse effect on data quality.
**See plan for further guidance if no laboratory criteria are provided.

5.5 BLANKS

NOTE: Blank analysis may not be required for all wet chemistry and miscellaneous methods (i.e., titrimetric determinations). Refer to the specified analytical method in the laboratory SOW to determine if a blank is required.

Blank analyses determine the existence and magnitude of contamination problems. A preparation or method blank is used to assess the level of contamination introduced to the analytical samples throughout the sample preparation and analysis process. If required by the analytical method, instrument blanks are analyzed following the ICV and CCVs throughout the analytical run. If problems are observed with any blank, associated data must be evaluated carefully to determine whether contamination has occurred, if there is an inherent variability in method baseline, or if the problem is an isolated occurrence.

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 nondedicated sampling equipment has been decontaminated properly and what, if any, carryover may arise between sampled locations. It has been EPA Region 4 data validation policy to evaluate the field blanks and equipment rinseate blanks as part of the validation process, but not to qualify the data based on these field samples.

5.5.1 Deliverables

- Blank results
- Sample preparation log and/or analytical run log
- Raw data for each blank (required for confirmation)

5.5.2 Frequency

Method blanks, if required by the method, typically are prepared and analyzed for each batch of 20 samples or less. The method blank must be similar matrix in each SDG. If required by the analytical method, instrument blanks are analyzed following initial calibration and at a frequency established by the method throughout the analytical run to follow CCVs.

5.5.3 Criteria

Target analytes should not be present in method or instrument blanks above the RL.

5.5.4 Data Verification

The data verifier shall verify the presence of the pertinent deliverables for blank analyses. If the required information is not present in the laboratory report, or if the frequency of analysis is not satisfied, the data verifier will contact the laboratory to obtain the omitted information. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If the information cannot be obtained, these occurrences are considered noncorrectable problems and will be identified as such on the data verification checklist. As this is a contract compliance issue, the occurrence should be communicated to the SMO and the data validator on the data verification checklist.

5.5.5 Data Validation

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

All laboratory blanks associated with the batch must be evaluated against the sample results in the batch. However, qualification should be applied only to those samples directly related to the affected blank (if more than one blank is used per batch). Sample results are not qualified based on field blank samples (field blanks or equipment rinseate blanks), but the data validation report can address field blank contamination if it is present.

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

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

If the blank result has an absolute value < RL, qualify the sample results < RL as nondetect (U). If the sample results are > RL, professional judgment of the reviewer is necessary to determine if the reported sample results are due to blank contamination.

If the reported blank result > RL, qualify all sample results > the RL but < 5 × the amount in any blank as nondetects “U”. Sample results > 5 × the blank concentration require no qualification.

If the blank result is negative, and the absolute value is > RL, all associated samples must be carefully examined. Sample results reported as positive, but < 5 × the absolute value of the blank shall be qualified “J,” and sample results reported as nondetects will be qualified “UJ.”

If gross contamination is present, the positive results must be evaluated carefully to determine if they are false positives. When gross contamination is observed in the method or instrument blank, qualify positive results < 10 × blank value "R." Results > 10 × the blank value should be qualified "J." Nondetects are unaffected by this condition.

Method Blanks				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Were method blanks and instrument blanks (if required) prepared and/or analyzed at the appropriate frequency?				*	*
2. Were sample results verified as uncorrected for blank concentrations?				J	NA
3. Are all sample results > RL and > 5 × the blank result? ***					
• Sample result is > RL and < 5 × the blank result				U	NA
• Sample result is < RL and < 5 × the blank result				U	NA
• Gross contamination				J/R	NA
4. Were negative concentrations in blanks evaluated?				J	NA
5. Was the presence of blank contaminants confirmed from raw data? (Applies to Level IV data only)				***	***

*Qualify only if the deviation indicates an adverse effect on data quality.
**Use professional judgment in qualifying data.
***When gross contamination is observed in the method or instrument blank, qualify positive results < 10 × the blank value "R." Results > 10 × the blank value should be qualified "J." Nondetects are unaffected by this condition.

5.6 LABORATORY CONTROL SAMPLE

The laboratory control sample (LCS) serves to monitor the overall performance of all steps in the analysis, including sample preparation and instrumental analysis.

NOTE: In very limited cases, an LCS is not required (e.g., coliform). However, the overwhelming majority of wet chemistry and/or miscellaneous methods require an LCS. Refer to the specific analytical method for guidance.

5.6.1 Deliverables

- LCS results
- Sample preparation log
- Analytical run log
- Raw data (required for confirmation—Level IV packages only)

5.6.2 Frequency

An LCS must be prepared and analyzed in accordance with the sample methodology. Typically, an LCS is prepared and analyzed with each batch of samples numbering 20 or less requiring sample preparation (i.e., digestion, filtration, extraction) before analysis. For methods not requiring sample preparation, an independent standard such as an ICV may be substituted for the LCS to monitor instrument performance.

5.6.3 Criteria

LCS %R must be within control limits specified by the analytical method, the standard supplier, or the laboratory. If laboratory-generated control limits or vendor-supplied limits are not provided, control limits for LCS %R of 80–120% shall be used.

5.6.4 Data Verification

The data verifier shall verify the presence of LCS results. If results are omitted from the laboratory report, the data verifier will contact the laboratory to obtain the omitted information. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If LCS analysis was required but not performed, this is considered a noncorrectable problem and shall be indicated on the data verification checklist. As this is a contract compliance issue, the occurrence should be communicated to the SMO and the data validator on the data verification checklist.

5.6.5 Data Validation

If laboratory-generated control limits are provided, qualify as follows:

- If LCS %R is within 20% of the laboratory's lower control limit, qualify detected results as estimated "J" and nondetect results as "UJ."

- If LCS %R is greater than laboratory's upper control limit, qualify detected results as estimated "J." Nondetect results are acceptable and require no qualification.

- If LCS %R is more than 20% lower than laboratory's lower control limit, qualify detected results as estimated "J" and nondetect results as rejected "R."

If laboratory-generated control limits are not provided, qualify as follows:

- If LCS %R = 50–79%, qualify detected results as estimated "J" and nondetect results as "UJ."

- If LCS %R > 120%, qualify detected results as estimated "J." Nondetect results are acceptable, and no qualification is required.

- If LCS %R < 50%, qualify positive results as estimated "J" and nondetect results as rejected "R."

Laboratory Control Sample				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have LCS results been included in the data package?				*	*
2. Was the LCS prepared and analyzed at the appropriate frequency?				*	*
3. Were LCS %R within acceptable limits? **				----	----
• Is %R > upper control limit?				J	NA
• Is %R < lower control limit?				J	UJ/R

*Qualify only if the deviation indicates an adverse effect on data quality.
**See plan for guidance if no laboratory criteria are provided.

5.7 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

Matrix spike/matrix spike duplicate (MS/MSD) data are generated to determine the precision and accuracy of the analytical method in the specific sample matrices. They provide a sample/project-specific measure of the method's ability to recover target analytes under real sample conditions.

NOTE 1: MS/MSD analyses may not be required for all wet chemistry/miscellaneous methods (e.g., gravimetric, titrimetric, coliform, ignitability, and others). Refer to the specific analytical method to determine the appropriateness of a MS/MSD.

NOTE 2: For a MS that does not meet the technical criteria, apply the action to all samples of the same matrix, if the data validator considers the samples sufficiently similar. The data validator will need to exercise professional judgment in determining sample similarity. The data validator 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., TSS, TDS, TOC, alkalinity or buffering capacity, reactive sulfide, anions) in determining similarity. The data validator should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the data package.

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

5.7.1 Deliverables

- MS/MSD results
- Sample preparation log
- Analytical run log
- Raw Data (required for confirmation)

5.7.2 Frequency

MS/MSD samples must be analyzed at a frequency of at least one pair per 20 field samples, and they must be prepared from the same or similar matrix for the samples they accompany. If multiple matrices are prepared together (e.g., water and soil) by the laboratory, individual MS/MSD samples must be prepared to reflect each matrix type.

5.7.3 Criteria

MS/MSD recoveries must be within control limits specified by the analytical method or those generated by the laboratory. This will be defined in the laboratory SOW. Absent predefined control limits 75–125% shall be used.

Precision for MSDs is measured in terms of relative percent difference (RPD). MSD precision must be within control limits specified by the analytical method or those generated by the laboratory. This will be defined in the laboratory SOW or project QAPP. In the absence of predefined control limits, ± 25% RPD for aqueous samples, and ± 35% RPD for soil/solid matrices shall be used for sample results > 5 × RL. If the sample results are < 5 × RL, use the criteria of ± RL for aqueous samples or ± 2× RL for soil samples.

5.7.4 Data Verification

Data verifier shall verify that MS/MSD samples were analyzed at the required frequency and that results are provided for each sample. If results are omitted from the laboratory report, the data verifier will contact the laboratory to obtain the omitted information. Upon receipt, this information will be placed in the data package for delivery to the data validator.

If results cannot be obtained or the frequency of analysis is not satisfied, these occurrences are considered noncorrectable problems and will be identified as such on the data verification checklist. As this is a contract compliance issue, the occurrence will be communicated to the SMO and data validator on the data verification checklist.

The laboratory is required to use a natural sample when preparing and analyzing MS/MSDs. If a field blank has been used for the MS/MSD, the data verifier will consult with the SMO to determine an appropriate course of action. Samples may require reanalysis to ensure project data is not affected by this action. If not, the issue will be identified as uncorrectable on the data verification checklist and feedback will be provided to project personnel and the laboratory to ensure this is not repeated.

5.7.5 Data Validation

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/laboratory control sample duplicate (LCSD) pair as a substitute to provide an evaluation of precision in the measurable range of the method.

The laboratory may also 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 is commonly 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 “J” and nondetects “UJ” unless other quality deficiencies are observed.

Recalculate one MS recovery from raw data. Equation D1 in Appendix C is used to calculate MS %R (Level IV only). If the MS/MSD or LCS/LCSD has been provided and recovery difficulties have been experienced, the following guidance shall be used for evaluating accuracy:

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

- If MS %R > 125%, qualify detected analytes “J” estimated. Nondetects do not require qualification.

- If MS %R is > 30% and < 75%, qualify detected analytes “J” estimated and nondetects “UJ” estimated.

- If MS %R is < 30%, qualify detected analytes “J” estimated and nondetects “R” rejected.

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

- If the RPD for water/liquid MS/MSD is > 25%, qualify associated detections "J" and nondetects "UJ."

- If the RPD for soil/solid matrices is > 35%, qualify associated detections "J" and nondetects "UJ."

Matrix Spike/Matrix Spike Duplicate				**Qualification Guidance**	
Validation Step	Yes	No	NA	Detects	Nondetects
1. Have MS/MSD results been included in the data package?				----	----
2. Were the MS/MSD analyzed at the appropriate frequency? *				----	----
3. Are MS and MSD percent recoveries within acceptance criteria? **				J	UJ/R
• Is %R > upper control limit?				J	NA
• Is %R < lower control limit?				J	UJ/R
4. Are all MS/MSD 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.

5.8 DUPLICATES

A laboratory duplicate sample typically 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 may also 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.

5.8.1 Deliverables

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

5.8.2 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.).

5.8.3 Criteria

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

- For sample concentrations > 5 × the RL, the laboratory duplicate precision as measured by RPD must be within ± 25% for aqueous samples. For solid matrices, the RPD must be within ± 25% (lab duplicate) or ± 35% (field duplicate). If the sample values are < 5 × the RL, RPD does not apply. Instead, the absolute difference between sample and duplicate must be < 5× the RL.

5.8.4 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/or field duplicate results. If the results 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 analytical 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.

5.8.5 Data Validation

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples to be sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, when determining similarity, 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., TSS, TDS, TOC, alkalinity or buffering capacity, reactive sulfide, anions]. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the duplicate 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 duplicate, and thus only the field sample used to prepare the duplicate sample should be qualified.

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

- 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, etc.) on one or more samples.

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

Laboratory and field duplicate qualification information is presented in Table 3.

Table 3. 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 control limits above 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.

5.9 SAMPLE RESULT VERIFICATION

If the laboratory has a high rate of manual transcription in generation of sample results, the project team may choose to manually recalculate sample results at a determined frequency. If sample results cannot be reproduced through manual calculation, contact the laboratory to resolve the problem. If calculations have been determined to be performed incorrectly such that reported results are incorrect, the data validator will make corrections manually during data validation. If consultation with the laboratory cannot resolve calculation anomalies, the data validator will use professional judgment to determine the effect on the data set. Data may be qualified "J" estimated or "R" rejected depending on the severity of the issue and the extent to which it impacts the data.

If results are to be manually recalculated from raw data, the following strategy is recommended:

- Examine raw data for anomalies.
- Verify from raw data two detected and nondetected results for each analyte and/or method of analysis (Level IV validation only).
- Confirm the initial and final sample volumes/weights used for sample analysis from sample preparation logs.

All analyses must fall within the instrument calibration range. If outside, confirm that the sample has been diluted and reanalyzed and that results are corrected for dilution factor(s).

Sample Result Verification			
Validation Step	Yes	No	NA
1. Did recalculation confirm reported results? If not, increase the frequency of recalculation until adequate confidence is gained in the reported results (Applies to Level IV only)			
2. Were reported results within the calibration range of the instrument?			
3. Were results from diluted samples corrected for the dilution factor?			

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 report (if applicable)

7. REFERENCES

NOTE: The most current versions of the references listed below should be utilized when using this plan for the data review, verification, and validation process.

EPA QA/G-4, *Guidance on Systematic Planning Using the Data Quality Objective Process*, February 2006.

EPA QA/R-5, *EPA Requirements for Quality Assurance Project Plans*, March 2001.

EPA-600/4-79-020, *Methods for Chemical Analysis of Water and Wastes*, March 1983.

EPA-540/R 10-011, USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review, January 2010.

SW-846 Final Update IV of the Third Edition, *USEPA Test Methods for Evaluating Solid Waste*, revisions through Update III, March 2009.

CP3-ES-5003, *Quality Assured Data*.

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 Matrix Spike/Matrix Spike Duplicate (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 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 attachment 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
Standard curve correlation coefficient	Quantitative uncertainty
Continuing calibration verification	Positive or negative bias
Method blank	Positive bias
Laboratory control sample	Positive or negative bias and precision
Matrix spike/matrix spike duplicate	Positive or negative bias and precision

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 Matrix spike percent recovery

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

where: SSR = Spiked Sample Recovery
SR = Sample Result
SA = Spike Added

C.2 Relative Percent Difference

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

where: R1 = first sample value (original)
R2 = second sample value (duplicate)

C.3 Laboratory Control Sample and Continuing Calibration Verification Percent Recovery

$$\%R = \frac{FOUND}{TRUE} x100$$

where: FOUND = Concentration (in µg/L for aqueous; mg/kg for solid) of each analyte measured in the analysis of LCS or CCV Solution.

TRUE = Concentration (in µg/L for aqueous; mg/kg for solid) of each analyte in the LCS or CCV source.

C.4 Sample Results—Refer to the specific analytical method for equations for calculation of sample results for soil and water.

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