

Hanford Analytical Services Quality Assurance Requirements Document

Volume 4: Laboratory Technical Requirements

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management



U.S. DEPARTMENT OF
ENERGY | Richland Operations
Office

P.O. Box 550
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CONTENTS

1.0	QUALITY ASSURANCE OBJECTIVES	1-1
1.1	DATA QUALITY OBJECTIVES	1-1
1.2	CLIENT DATA QUALITY REQUIREMENTS.....	1-2
1.2.1	Precision.....	1-2
1.2.2	Accuracy	1-3
1.2.3	Comparability	1-3
1.2.4	Completeness	1-3
1.2.5	Representativeness.....	1-3
2.0	SYSTEMS QUALITY ASSURANCE.....	2-1
2.1	TECHNICAL SYSTEMS.....	2-1
2.2	PHYSICAL FACILITIES SYSTEMS AND LABORATORY EQUIPMENT	2-1
3.0	SAMPLE CUSTODY AND HANDLING	3-1
3.1	CHAIN-OF-CUSTODY DEFINITION.....	3-1
3.2	HOLDING TIMES	3-1
3.3	SAMPLE RECEIVING	3-1
3.4	SAMPLE LOG-IN AND TRACKING.....	3-3
3.5	LABORATORY INTERNAL CHAIN-OF-CUSTODY	3-4
3.6	SAMPLE DISPOSITION	3-4
4.0	CALIBRATION	4-1
4.1	CALIBRATION RECORDS	4-1
4.2	BALANCES, THERMOMETERS, AND PIPETTES	4-2
4.3	GENERAL REQUIREMENTS FOR STANDARDS, REAGENTS OR OTHER MATERIALS CRITICAL TO LABORATORY ANALYTICAL PROCESSES.....	4-3
4.4	CALIBRATION OF LABORATORY MEASUREMENT SYSTEMS	4-4
4.4.1	Radionuclide Analysis	4-5
4.4.2	Inorganic Analysis	4-13
4.4.3	Organic Analysis.....	4-16
4.4.4	Physical Testing.....	4-20
5.0	DATA COLLECTION, REDUCTION, AND REPORTING	5-1
5.1	DATA COLLECTION	5-1
5.2	DATA REDUCTION	5-2
5.2.1	Significant Figures	5-2
5.2.2	Rounding-Off Methods.....	5-3
5.2.3	Data Review.....	5-3
5.3	DATA REPORTING	5-4
5.3.1	Data Reporting Documentation	5-4
5.3.2	Immediate Reporting	5-5

6.0	QUALITY CONTROL.....	6-1
6.1	GENERAL LABORATORY QUALITY CONTROL.....	6-1
6.1.1	Distilled or Deionized Water	6-2
6.1.2	Compressed Gases	6-2
6.1.3	Standards.....	6-2
6.1.4	Reagents.....	6-2
6.1.5	Labware.....	6-3
6.1.6	Glassware Cleaning	6-3
6.1.7	Good Housekeeping.....	6-3
6.2	PREPARATIVE TECHNIQUES FOR RADIOCHEMISTRY	6-3
6.2.1	Preparation/Separation Batch.....	6-5
6.2.2	Preparation Blank or Method Blank	6-5
6.2.3	Laboratory Control Sample or Blank Spike.....	6-6
6.2.4	Matrix or Post Spike	6-7
6.2.5	Laboratory Sample Duplicate or Matrix Spike Duplicate	6-8
6.2.6	Tracer	6-9
6.2.7	Carrier	6-10
6.3	RADIOANALYTICAL TECHNIQUES	6-11
6.3.1	Counting Sequence	6-11
6.3.2	Verification of Calibration.....	6-11
6.3.3	Counter Control Source	6-12
6.3.4	Backgrounds	6-13
6.4	INORGANIC PREPARATIVE TECHNIQUES.....	6-13
6.4.1	Preparation Batch.....	6-14
6.4.2	Preparation Blank (Method Blank).....	6-15
6.4.3	Laboratory Control Sample or Blank Spike.....	6-16
6.4.4	Matrix Spike.....	6-16
6.4.5	Laboratory Sample Duplicate or Matrix Spike Duplicate	6-17
6.5	INORGANIC ANALYTICAL TECHNIQUES	6-18
6.5.1	Analytical Run or Sequence.....	6-18
6.5.2	Initial Calibration Verification.....	6-24
6.5.3	Continuing Calibration Verification	6-24
6.5.4	Initial and Continuing Calibration Blanks	6-24
6.5.5	Internal Standards	6-25
6.5.6	Low-Level Standard.....	6-25
6.5.7	Interference Check Standards	6-25
6.5.8	Post-Digestion Spike.....	6-26
6.5.9	Serial Dilution.....	6-26
6.5.10	Method of Standard Additions.....	6-27
6.6	ORGANIC PREPARATIVE TECHNIQUES	6-27
6.6.1	Preparation Batch.....	6-28
6.6.2	Preparation Blank (Method Blank).....	6-29
6.6.3	Laboratory Control Sample or Blank Spike.....	6-30
6.6.4	Matrix Spike.....	6-30

6.6.5	Laboratory Sample Duplicate or Matrix Spike Duplicate	6-31
6.6.6	Surrogates	6-32
6.7	ORGANIC ANALYTICAL TECHNIQUES	6-32
6.7.1	Analytical Sequence (Run)	6-33
6.7.2	Initial Calibration Verification.....	6-33
6.7.3	Continuing Calibration Verification	6-35
6.7.4	Continuing Calibration Blank.....	6-36
6.7.5	Internal Standards	6-36
6.7.6	Low-Level Standard.....	6-36
6.7.7	Tentatively Identified Compounds	6-37
6.8	PHYSICAL TESTING	6-37
7.0	COMMON DATA QUALITY CALCULATIONS.....	7-1
7.1	PRECISION.....	7-1
7.1.1	Relative Standard Deviation	7-1
7.1.2	Relative Percent Difference	7-2
7.2	ACCURACY	7-2
7.2.1	Method Accuracy Based on Sample Spike.....	7-2
7.2.2	Method Accuracy Based on Standard.....	7-2
7.3	YIELD RECOVERY (RADIOCHEMISTRY ONLY)	7-3
7.4	MEASURES OF AGREEMENT	7-3
7.4.1	Percent Difference	7-3
7.4.2	Bias	7-4
7.4.3	Mean Difference	7-4
7.5	DETECTION LIMIT CONSIDERATIONS	7-5
7.5.1	Inorganic and Organic Methods.....	7-5
7.5.2	Radiochemistry Methods	7-9
7.6	UNCERTAINTY	7-12
7.7	CONTROL CHARTS.....	7-13
8.0	DATA ASSESSMENT AND VALIDATION	8-1
8.1	DATA ASSESSMENT PROCESS.....	8-1
8.2	PLANNING CONSIDERATIONS	8-1
8.3	ASSESSMENT AND VALIDATION	8-2
8.4	DATA USABILITY	8-4
8.4.1	Example 1 – Unqualified Method Deficiencies.....	8-4
8.4.2	Example 2 -- Data Qualified But Usable	8-5
9.0	REFERENCES AND BIBLIOGRAPHY	9-1

APPENDICES

A SUMMARY OF THE DATA QUALITY OBJECTIVE PLANNING PROCESS A-1

B U.S. ENVIRONMENTAL PROTECTION AGENCY, CONSENSUS, AND
U.S DEPARTMENT OF ENERGY METHODSB-1

TABLES

Table 4-1. Minimum Requirements of Calibration, Background, and Counter Control for
Alpha and Beta Counting..... 4-7

Table 4-2. Minimum Requirements of Calibration, Background, and Counter
Control for Gamma Spectrometry 4-8

Table 4-3. Minimum Requirements of Calibration, Background, and Counter Control for
Alpha Spectrometry. 4-9

Table 4-4. Minimum Requirements of Calibration, Background, and Counter Control for
Beta Spectrometry and Kinetic Phosphorescence 4-10

Table 4-5. Minimum Calibration Requirements for Inorganic Analyses 4-13

Table 4-6. Minimum Requirements for Gas Chromatograph/Mass Spectrometer
Systems 4-16

Table 4-7. Minimum Requirements of Calibration and Calibration Verification for Gas
Chromatograph System 4-18

Table 4-8. Minimum Calibration Requirements for Total Organic Carbon, Total
Inorganic Carbon, and Total Carbon Analysis Using Different Instruments. 4-20

Table 4-9. Minimum Calibration Requirements for Thermogravimetric Analysis,
Differential Thermal Analysis/Thermal Gravimetry, and Differential
Scanning Calorimetry. 4-20

Table 6-1. Preparative Requirements for Radiochemistry Quality Control..... 6-4

Table 6-2. Preparative Requirements for Inorganic Quality Control..... 6-13

Table 6-3. Analytical Requirements for Inorganic Quality Control 6-19

Table 6-4. Preparative Requirements for Volatile, Semi-Volatile, and
Gas Chromatography Quality Control..... 6-27

Table 6-5. Analytical Requirements for Volatile Quality Control (Gas
Chromatography/Mass Spectrometry)..... 6-34

Table 6-6. Analytical Requirements for Semi-Volatile Quality Control (Gas
Chromatography/Mass Spectrometry)..... 6-34

Table 6-7. Analytical Requirements for Gas Chromatography 6-35

Table 6-8. Analytical Requirements for Total Carbon, Total Inorganic Carbon, and Total Organic Carbon Quality Control 6-35

Table 6-9. Physical Testing Quality Control (Differential Scanning Calorimetry, Thermogravimetric Analysis, and Differential Thermal Analysis/Thermogravimetric Analysis)..... 6-38

LIST OF TERMS

ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
BS	Blank Spike
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CCB	Continuing Calibration Blank
CCS	Counter Control Source
CCV	Continuing Calibration Verification
CF	Calibration Factor
CFR	Code of Federal Regulations
DL	Detection Limit
DLR	Decision-Level Count Rate
DLV	Detection Limit Verification
DOE	U.S. Department Of Energy
DQO	Data Quality Objective
DQR	Data Quality Requirement
EPA	U.S. Environmental Protection Agency
EQL	Estimated Quantitation Limit
FWHM	Full Width Half Maximum
GC	Gas Chromatograph
HASQARD	Hanford Analytical Services Quality Assurance Requirements Document
IC	Ion Chromatography
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ICV	Initial Calibration Verification
ID	Identification
IDL	Instrument Detection Limit
LCS	Laboratory Control Sample
LOQ	Limit of Quantitation
MDA	Minimum Detectable Activity
MDC	Minimum Detectable Concentration
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
N/A	Not Applicable
NIST	National Institute of Standards and Technology
PDS	Post-Digestion Spike
PIC	Positively Identified Compound
PQL	Practical Quantitation Limit
QA	Quality Assurance
QC	Quality Control
QL	Quantitation Limit
RCRA	Resource Conservation and Recovery Act Of 1976
RF	Response Factor

RPD	Relative Percent Difference
RSD	Relative Standard Deviation
TIC	Tentatively Identified Compound
TPU	Total Propagated Uncertainty
VOC	Volatile Organic Compound

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1.0 QUALITY ASSURANCE OBJECTIVES

Quality Assurance (QA) objectives provide a set of recognized parameters to monitor and to quantify performance of an analytical measurement. This document provides specific criteria for QA objectives to ensure that laboratories engaged in compliance activities supporting the U.S. Department of Energy (DOE), Richland Operations Office and Office of River Protection maintain a uniform standard of performance.

1.1 DATA QUALITY OBJECTIVES

The primary responsibility for identifying data quality requirements (DQRs) lies with the client or data user. The client or data user is also responsible for communicating this information to the organization or staff responsible for performing the work. The communication process should be such that it allows the laboratory to understand and successfully meet client DQRs and comply with applicable regulations. Basic information about the nature of the sample(s) and the use of the data should be discussed and agreed on by the laboratory and the client before sample collection. This information should be provided through a formal data quality objective (DQO) process (see Appendix A). In the absence of a documented DQO process, as a minimum, the laboratory and the client shall agree on the required precision, accuracy, and sensitivity (e.g., instrument detection limit [IDL], method detection limit [MDL], and minimum detectable concentration [MDC]). Also, the following sample-specific criteria should be provided or agreed on and documented before the laboratory begins work:

- Applicable regulatory requirements such as chain-of-custody, holding times, and quality control (QC) specifications.
- Process knowledge, sample source, and sample conditions known to the client that could impact the laboratory worker's safety.
- Handling of radioactive samples in the transport process and in the laboratory.
- Estimated number and matrix of samples.
- Sample handling relative to a specific sample or matrix.
- Procedures and analyte lists for sample analysis – the analyte list should also specify whether or not tentatively identified compounds (TICs) are required.
- QC sample frequency, type, and acceptance criteria.
- Expected dates of sample receipt, sample preservation, delivery methods, storage and container types and volumes, and holding times by method.
- Format, content of sample analysis reports, and format of electronic data deliverables if requested.

- Turnaround time (from date of sample receipt to date of data delivery) in the laboratory.
- Name, address, telephone number of client, and laboratory contacts responsible for the project, and information to establish electronic data transfer (e.g., type of software, file format).
- Methods for reporting, resolving, and documenting anomalies and nonconformances from sample receipt to final reporting to the client (e.g., either stop work or revision to the original work requests could be used for nonconforming samples when submitted to the laboratory).
- Return of samples and disposition of waste.

The laboratory shall have a system to notify and explain any unique requirements to all staff performing work for the client. Unique requirements are those that differ from the procedures described in this document and in the laboratory procedures.

The laboratory shall notify the client when situations, such as anomalies and nonconformances, occur.

The laboratory shall have a process for documenting resolution of client complaints or issues. The process shall include documenting the complaint or the issue, the client contact, and the date the contact was made. All subsequent information that resolves the complaint or issue shall be maintained by the laboratory. The laboratory shall track the complaint or the issue from receipt to resolution.

1.2 CLIENT DATA QUALITY REQUIREMENTS

Five parameters are often used by the client to define project DQRs: precision, accuracy, completeness, comparability, and representativeness. Of these, the precision, accuracy, and representativeness have direct impacts on data quality (see Section 6.0 for limitations associated with precision and accuracy). The client is responsible for ensuring that adequate sample material is available and that appropriate sampling techniques are administered to meet their DQOs. The laboratory is responsible for using proper protective sample-handling protocols to produce data of a quality that meets the clients' DQOs. The laboratory and the client share responsibility for selecting appropriate sample preparation and analytical techniques. The precision and accuracy requirements shall be agreed on by the laboratory and the client and should be based on the uncertainty of both the sampling and the analytical effort.

1.2.1 Precision

Precision represents a measure of the degree of reproducibility of measurements under prescribed similar conditions. Sample precision is calculated on the basis of duplicate analyses. Acceptance criteria shall be established for each analyte and each analyte method and shall be agreed on by the laboratory and the client.

1.2.2 Accuracy

Accuracy represents the degree to which a measurement agrees with an accepted reference or true value. Sample accuracy is assessed using the percent recovery of a spiked sample. Acceptance criteria shall be established for each analyte and each analyte method and shall be agreed on by the laboratory and the client.

1.2.3 Comparability

Comparability is the confidence with which one data set can be compared to another. For each analyte, comparable precision and accuracy depend on the method and sample matrix. To be comparable, similar precision, accuracy, and detection limits shall be achieved on samples with similar matrices using similar methods. Factors such as analytical method selected, detection limits or uncertainty, precision, accuracy, and matrix effects should be considered when data is to be compared between multiple laboratories. Furthermore, split samples or known standards may be used for comparability of different methods.

1.2.4 Completeness

Completeness is a measure of the amount of usable and/or valid data obtained from a measurement system compared to the total amount of data requested. Completeness can be used to evaluate the amount of data produced that meets the client's requirements (e.g., accuracy, precision). In some cases, data may not meet all the requirements but may still be used for qualitative information as an indicator of the presence or absence of a parameter. A clear definition of completeness based on the types of qualification allowed should be agreed on by the laboratory and the client. Developing a requirement for critical samples that differ from other samples may also be useful.

1.2.5 Representativeness

Representativeness is the degree to which data accurately and precisely represents a characteristic of a population, a parameter variation at a sampling point, a process condition, or an environmental condition. Representativeness of a population or an environmental condition depends heavily on sampling and is addressed in other documents (which are not in the scope of this document). Analytical data should not be taken as the sole indicator of representativeness of the sample process condition. The methods should be assessed after accumulation of sufficient data to represent the same population.

The laboratory is responsible for handling and preparing the sample properly to maintain representativeness of the sample. Representativeness may be obtained by proper homogenization or sub-sampling. If different phases are apparently visible in the sample, the laboratory should consult with the client to determine sub-sampling and homogenization needs.

If sub-sampling is needed, the DQRs should be re-evaluated to determine if sub-sampling impacts the ability to meet representativeness requirements and if a different methodology is required for preparation and analysis. Both the laboratory and the client should recognize that representativeness of the sample may be impacted by difficulty in, or inability to, achieve homogeneity.

2.0 SYSTEMS QUALITY ASSURANCE

A number of systems exist within a laboratory. These systems need to function properly to produce and document the high level of quality needed in the final product. These systems are the software systems, administrative systems, technical systems, and physical facilities systems. Administrative controls shall be established for each system.

Technical systems and physical facilities are discussed in this section. Software systems are discussed in Volume 1, Section 7.0.

2.1 TECHNICAL SYSTEMS

Technical systems assure that the techniques used are applicable and properly applied. These systems include sample exchanges, standards programs, control of standards, reagents, reference materials or other media potentially impacting the quality of reported results, analytical instrumentation and equipment, data reduction and reporting, data verification and validation, and technical audits. Procedures for documenting the above systems, including required associated precision and accuracy criteria as appropriate, shall be established.

2.2 PHYSICAL FACILITIES SYSTEMS AND LABORATORY EQUIPMENT

Proper facility design and maintenance can help alleviate problems associated with data generation. The following, at a minimum, shall be documented or addressed in the laboratory QA Plan, laboratory procedures, or facility operations procedures:

- Ventilation, with air exchange rates and pressure differential between work area, suitable working environment (e.g., lighting, temperature control), stable power sources, and radio frequency shielding.
- Adequate space for laboratory functions so that laboratory activities do not adversely affect analyses.
- Specialized equipment (e.g., an acid hood or glove box), where required.
- Water purification (see Section 6.1.1).
- Adequate analytical instrumentation sufficient to perform the scope of work.
- Documentation of instrumentation configuration and settings.
- Preventive maintenance schedules for equipment (see Volume 1, Section 9.0).
- Adequate storage with temperature control and temperature monitoring to provide for security of samples and to prevent contamination, degradation, or misidentification of samples. Daily monitoring of temperatures in refrigerators and freezers used for sample

storage shall be performed and documented. For temperature monitoring, “daily” refers to calendar days, not working days. Temperature monitoring data loggers are acceptable provided they have the capability of providing notification of an out of control event to responsible individual(s) during routine and non-routine work periods. Corrective actions shall be performed in the event of an out of control condition or catastrophic failure of a refrigerator or freezer. The requirement for daily monitoring of temperature for refrigerators and freezers does not apply to refrigeration and freezer units where samples are not being stored.

- Adequate storage areas for reagents, solvents, standards, and reference materials to prevent cross-contamination, degradation, or loss.
- Proper facility access control maintained in a manner to preclude unauthorized access.
- Adequate facilities for collection, storage, and disposition of sample wastes (with facilities operated to minimize environmental contamination).
- Waste management facilities to comply with applicable federal, state, and local regulations.

3.0 SAMPLE CUSTODY AND HANDLING

This section identifies requirements for chain-of-custody to be maintained between the sample collection and the laboratory receiving area, and specifies requirements for internal custody in the laboratory. Internal custody refers to maintaining custody as a sample container is removed from storage and moved within the laboratory for analysis. Internal custody shall be maintained until final disposition or return of the sample to the client. The scope of this document is limited to the custody requirements beginning with laboratory sample receipt.

3.1 CHAIN-OF-CUSTODY DEFINITION

The purpose of the chain-of-custody is to document sample possession and to demonstrate that the sample was maintained in a controlled and unaltered state. This demonstration supports the interpretation of the sample results and may be required in legal proceedings, and for a number of other purposes.

Custody in the laboratory is defined as secured to prevent tampering and may be accomplished by having the sample in one of the following situations: (1) in actual physical possession, (2) in view of the sample custodian after being in physical possession, (3) in a locked area, or (4) in a designated secured area (e.g., accessible only to authorized personnel).

3.2 HOLDING TIMES

Many analytes regulated under environmental statutes (e.g., the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* [CERCLA], and the *Clean Water Act of 1972*) require adherence to holding time requirements. Regulatory holding time begins at sample collection. Some regulatory holding times include collection through final analysis; others segregate the time between collection through preparation, and preparation through analysis. The U.S. Environmental Protection Agency (EPA) has set maximum holding times for most analytes regulated under the *Resource Conservation and Recovery Act of 1976* (RCRA) (EPA SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*). The aqueous holding time requirements are consistent with those in the *Clean Water Act* in Title 40, Code of Federal Regulations (CFR), Part 136 (40 CFR 136), "Guidelines Establishing Test Procedures for the Analysis of Pollutants."

The laboratory and the client shall agree on the necessity of applying regulatory holding times before sample collection. The client shall be responsible for the timely delivery of samples to the laboratory enabling the laboratory to meet holding time requirements. If the laboratory is unable, for any reason, to meet prescribed holding times, the laboratory shall notify the client in writing as soon as possible.

3.3 SAMPLE RECEIVING

The laboratory shall have a procedure, or series of procedures, which address sample receipt. The laboratory shall utilize a permanent chronological record, such as a log book or electronic

database, to document receipt of all sample containers. This sample receipt log shall record the following:

- Client/project name
- Date and time of laboratory receipt
- Identification of the person making the entries.

The following actions shall be addressed in the laboratory procedure(s):

- Document transferring samples to the laboratory. When received from a common carrier, a copy of the shipping document shall become part of the permanent laboratory record.
- Verify that the outermost sample container(s) is not damaged.
- Verify that the outermost sample seal(s) is intact, if present.
- Assure that radiation control procedures are followed for receipt, when applicable.
- Verify that the chain-of-custody documentation is complete and legible. The documentation shall include the following information:
 - Client/Project or location name/number
 - Client sample number
 - Date, time, and location (or traceable reference thereto) of sample collection.
 - Signatures and printed names of individuals involved in sample transfer and storage, to include all dates, times, and locations as applicable.
- Verify the temperature of the cooler when it is received where specified by the procedures or protocols, and note any deviations.
- Record the results of all sample receipt checks.
- Verify, if required, field preservation has been performed on water samples (except for samples received for analyses for volatile analytes) using readily available techniques such as pH. Document unpreserved samples on the custody form, sample check-in documentation, or in the laboratory's nonconformance tracking system.
- Verify that the collection date and date of laboratory receipt are within method- or project-specific holding time requirements.
- Notify laboratory staff as soon as possible when the sample holding time is less than 48 hours.

- Verify that the client's sample numbers on the chain-of-custody documentation match those on the sample containers.
 - Evaluate the condition of sample containers.
 - Note anomalies either on the custody form or on sample receiving documentation.
 - If shipping containers and/or individual sample containers are submitted with sample custody seals and any seals are missing, the sample custodian shall note this on the sample receiving documentation.

Laboratory procedure(s) shall provide for timely notification to the client by telephone, facsimile, or electronic mail of sample received, any nonconformance that will impact the laboratory's ability to meet agreed on DQRs, or nonconformances potentially impacting documentation of chain-of-custody before proceeding with further work. All nonconformances noted during sample receipt shall be communicated to the client for resolution. The laboratory shall maintain the documentation supporting such notifications, which may include copies of the telephone logs, facsimiles, or electronic mail. Nonconformance notification and client responses shall be documented, tracked through closure, and kept on file in the laboratory.

If prompt client response (within two business days) is not received to a notification of nonconformance, the laboratory can proceed at its discretion to analyze the samples. All actions and decisions must be documented in the project file and include a summary of the nonconformances and corrective actions in the narrative accompanying the final report (upon client's statement of work).

When sample receipt is completed and samples are accepted for analysis, the laboratory shall initiate internal chain-of-custody in accordance with Section 3.5 and begin analytical activities.

3.4 SAMPLE LOG-IN AND TRACKING

Upon receipt of samples in the laboratory, the following shall be completed as part of the sample log-in and tracking process, and shall be addressed in appropriate laboratory procedures:

- Having accepted the samples, the laboratory shall maintain custody of the samples during the laboratory log-in and sample distribution processes. The samples shall be secured in a designated refrigerated or other storage location, as appropriate for the sample container and material type.
- The laboratory shall ensure that the records documenting possession and transfer are properly completed and placed in the laboratory records system.
- The laboratory shall maintain a cross-reference to correlate the laboratory's sample identification to the client's sample identification.

- Each sample or sub-sample shall be given a unique identifier regardless of its resample status. Every sample, sample replicate, sub-sample, and sample extract shall be identified in a manner that allows traceability to the parent sample number.
- Information related to storage, preservation, holding time, and requested analysis shall match the work-authorizing document (e.g., tank characterization plan).
- Any safety hazards communicated by the client shall be documented and communicated to the laboratory staff.
- A declaration of the radiation level shall accompany those samples that contain radioactive materials.
- A system shall be in place to allow tracking of samples and holding times. The system shall allow the laboratory to assess if holding times shall be met or exceeded, and to assess the number of samples available for analysis.

3.5 LABORATORY INTERNAL CHAIN-OF-CUSTODY

The laboratory approach taken to address internal chain-of-custody of samples shall be documented and implemented through approved internal procedures. Once samples are in the laboratory, sample custody shall be controlled. The location of all samples and the person in control of the samples shall be traceable from the time samples are received at the laboratory until final disposition. Traceability within the laboratory may be electronic, based on personnel bar codes, passwords, or other secure techniques. Tracking records shall include, by direct entry or linkage to other records, the date and time of each transfer.

In a laboratory restricted to authorized personnel only, the entire laboratory is considered a secured area, provided the laboratory has developed and implemented procedures that address laboratory security.

Shipping records shall be maintained. If a chain-of-custody failure is detected, the client shall be contacted for resolution.

3.6 SAMPLE DISPOSITION

The sample disposition procedure shall include the following:

- Return of samples to the client or disposition through other laboratory waste management systems
- Maintenance of records that identify the date and method of sample disposition
- Provisions to ensure all federal, state, and local disposal regulations have been met
- Provisions for sample archiving.

4.0 CALIBRATION

This section describes calibration and/or activities associated with calibration requirements for laboratory measurement systems and specifications for standards that are used for calibration. The performance of the laboratory measurement system, in general, is controlled through calibration and monitored by continuing verification of calibration.

Analytical measurements are made using systems that include sample handling, sample preparation, and measurement processes. Data generated for clients shall be acquired using calibrated equipment. Documentation of calibration must be maintained such that it is traceable to the measurement system and results generated from that system. Equipment not calibrated by the user (e.g., an analytical balance) that is out of calibration must be clearly identified to prevent use. Ancillary data (e.g., temperature, pressure, humidity, particle size, volumetric capacity, mass, and flow rate) may also be needed, requiring accurately calibrated instrumentation for their measurement. Accordingly, any of the instruments, standards, and methods used to generate information essential to generation of final results shall be calibrated to assure that their accuracy is within acceptable limits. Analysis shall not be initiated until a valid calibration is achieved.

Results reported from a measurement system must be within the working range of the calibration. That is, the standard concentrations must bracket the field sample and QC sample concentrations unless otherwise allowed by the analytical method (e.g., inductively coupled plasma (ICP)/atomic emission spectrometry). If multiple calibration curves are used, analytical QC must be performed for each curve. Over-range samples are diluted or otherwise re-analyzed within the calibration range of the measurement system or, when necessary, reported using defined qualifiers to denote increased quantitative uncertainty.

Requirements for calibration are different between radionuclide, inorganic, and organic analyses because of instrumentation characteristics and stability. This is primarily due to long-term (radiochemical) versus short-term (inorganic and organic) system stability. The detectors used within these chemical classes also have different calibration requirements based on their operating characteristics. It is inappropriate and unnecessary to impose the more frequent calibration requirements of inorganic and organic calibration and initial calibration verification (ICV) on radiochemical procedures. Care must also be taken within a class of analysis to apply method-specific procedures properly or risk inaccurate calibration. The requirements between and within chemical classes of analysis are discussed in the subsections that follow.

If more or less stringent requirements are necessary to meet project objectives, the variances shall be implemented according to the DQRs agreed to and documented by the laboratory and the client (Section 1.0).

4.1 CALIBRATION RECORDS

The laboratory shall keep a record of raw calibration data for all methods. Calibration records (e.g., initial calibration, ICV, and continuing calibration verification [CCV]) shall include the raw calibration data, associated reports, date of analysis, and analyst's name or initials, at a

minimum. Calibration data shall be traceable to the standards used. All samples analyzed shall be traceable to the calibration under which the results were produced. Sample analysis can only proceed when measurement systems are calibrated. These records shall be maintained according to Volume 1, Section 6.0.

4.2 BALANCES, THERMOMETERS, AND PIPETTES

All balances, and any thermometers, pipettes, and automatic sample dispensers used for quality affecting measurements, shall be uniquely identified. Calibration records of measurement devices (e.g., laboratory balances and thermometers for critical mass and temperature measurements) shall be maintained. All analytical balances shall be calibrated annually, at a minimum, by an approved metrology organization. An approved metrology organization is one that has been selected on the basis of specified criteria consistent with metrology standards for the calibration of balances. These records shall contain the date of calibration, initials of the person performing the calibration, the identity of the device or serial number, and the date the calibration expires. Balance identification and calibration expiration information shall be affixed on or near the balance. Balances shall be located in an area where the environment has little or no effect on measurement accuracy.

Acceptable balance calibration shall be verified and documented daily when in use. Balance check weights shall be at a minimum:

- Inherently stable in a laboratory atmosphere
- Uniquely identified with documented masses determined relative to National Institute of Standards and Technology (NIST) traceable weights
- Verified and documented at least annually to ensure stability.

For balance verification, check weight values shall be established and verified to at least the readability of the balance to which they will be assigned, preferably to 10 percent of the balance readability. For example, if a balance reads to 0.1 gram, check weight values should be established (known) to 0.01 gram. Daily checks shall include verification by bracketing the expected use range, or the verification shall include checking at approximately 2/3 (67 percent) of the balance capacity.

The accuracy of thermometers and thermocouples used for critical temperature measurements (e.g., refrigerator temperature for sample storage, total dissolved solids analysis) shall be verified annually by comparing readings of such devices with the readings of a NIST traceable factory-certified thermometer. If radiological conditions limit comparison to an NIST traceable thermometer, then an alternate check process (e.g., check at steam point, ice point, or comparison to some other known temperature reference) may be used in lieu of the NIST comparison.

It is considered good laboratory practice that mechanical volumetric dispensing devices used for quantitative measurements be verified daily or prior to use to ensure acceptable performance. Daily, before use, single-delivery volume checks shall be performed and documented. Unless

practical concerns preclude this practice (e.g., radiological work environments), volume checks shall be performed by delivery weight. Alternate volume check methodology shall be defined by procedure. Glass microliter syringes do not require daily or quarterly verification but must come with a certificate attesting to established accuracy or the accuracy must be initially demonstrated and documented by the laboratory.

4.3 GENERAL REQUIREMENTS FOR STANDARDS, REAGENTS OR OTHER MATERIALS CRITICAL TO LABORATORY ANALYTICAL PROCESSES

The following standard specifications shall be used unless otherwise specified in Section 4.4.

Standards used for calibration of measurement systems or preparation of other QC standards (e.g., laboratory control sample [LCS], surrogate spiking solutions, matrix spiking solutions) shall be traceable to a nationally or internationally recognized standard agency (e.g., NIST) source or measurement system, if reasonably available. When a nationally or internationally recognized standard material is unavailable or its purchase is impractical, the laboratory shall:

- Purchase standard material from a reliable source, or
- Establish or define an alternate calibration protocol (e.g., use of surrogate radioisotope for the unavailable material).

The laboratory shall have procedures/documents in place to determine the acceptability of such non-routine materials. Purchased standards shall be accompanied by a Certificate of Analysis or record that includes the vendor, lot number, purity, date of preparation and/or expiration, and concentration or activity of the standard material. The accuracy and traceability of all working standards to appropriate primary grade standards or the highest quality standards available shall be documented.

The laboratory shall retain records for all standards, reagents, reference materials, or other media potentially impacting the quality of reported results. These records shall allow for traceability to all appropriate calibration and sample analysis activities. Traceability to purchased stock reagents or materials used directly need only identify manufacturer and lot number.

The laboratory shall address recommended storage conditions and document an expiration date, after which the material shall not be used unless its reliability is re-verified. Standards shall be stored in a manner to prevent cross-contamination with samples.

A program and the criteria used to verify or re-verify standards, reagents, reference materials, or other media potentially impacting the quality of reported results shall be defined and documented to assure that acceptable accuracy is maintained.

Laboratory prepared standards shall be traceable to the primary standard documentation. At a minimum, the following information shall be maintained regarding laboratory prepared standards, reagents, reference materials, or other media potentially impacting the quality of reported results:

- Name of preparer
- Date prepared
- Standard identification
- Traceability to purchased stocks or neat compounds
- Dilution documentation, including volume/weight of standards, final volume, etc.
- Traceability to any critical equipment used (e.g., balance IDs, pipette IDs)
- Final concentration or activity
- Reference to the method of preparation (e.g., procedure ID)
- Expiration date or shelf life (if applicable).

Containers for standards, reagents, reference materials, or other media potentially impacting the quality of reported results shall be labeled in a way to ensure traceability to preparation/certification documentation. The minimum amount of information required to be on each standard label includes:

- Expiration date or shelf life (if applicable)
- A unique identifier that allows traceability to the applicable standards preparation documentation.

The expiration date of a laboratory prepared standard shall not exceed the expiration date of the primary standard. Expired standards shall not be used unless their reliability is verified by the laboratory. If expired standards are not recertified, the laboratory shall remove the standard or clearly designate it as acceptable for qualitative purposes only. A standard is considered valid for quantitative purposes up to the date listed as the expiration date. When the expiration date is expressed as a month/year, the last valid date for use is the last day of the month listed.

4.4 CALIBRATION OF LABORATORY MEASUREMENT SYSTEMS

The calibration process correlates instrument response to an established concentration or characteristic. Calibration procedures shall be established by the laboratory and shall consider the manufacturer's recommendations and the requirements specified in this section. Instrument operational parameters (e.g. temperature, temperature change rate, flow, mobile phase carrier, solvent, counting time, attenuation, detector voltage) shall consider the manufacturer's recommendations or requirements and will be consistent, as applicable to the analytical method, between client samples, laboratory QC samples, and calibration standards. Specific requirements or considerations for calibration and calibration standards used for radiochemistry, inorganic, organic, and physical testing laboratory measurement systems are defined in Sections 4.4.1, 4.4.2, 4.4.3, and 4.4.4, respectively.

The ICV checks the accuracy of the calibration and the standards used for that purpose. A level of independence shall exist between the materials used for calibration and for ICV when such materials are available. When an independent source is not available, the laboratory should attempt to purchase an alternate lot of the same material.

The CCV checks the stability of the original calibration over time. This standard may be from the same source as that used for either calibration or ICV.

The minimum requirements of calibration, frequency, and acceptance criteria for laboratory measurement systems are presented in Table 4-1 through Table 4-9. Where a Hanford Site activity requires using a specific regulatory method (e.g., permits, National Pollutant Discharge Elimination System), and the regulatory method is in conflict with the *Hanford Analytical Services Quality Assurance Requirements Document* (HASQARD), the regulatory method shall take precedence. Where no conflict exists or no requirements are specified, all other sections of the HASQARD would apply.

Records associated with instrument calibration and control shall identify the following:

- Test type
- Identification of instrument calibrated
- Date of test
- Name of person performing the test
- Results and their acceptability
- Corrective actions taken when unacceptable.

The laboratory is required to take corrective action when measurement systems fail calibration QC criteria, as demonstrated by the procedures discussed in Section 6.0. When recalibration is required at an unusual and/or increasing frequency, see Volume 1, Section 5.0 for corrective actions.

4.4.1 Radionuclide Analysis

Radionuclide analysis is defined as the measurement of nuclear decay through counting alpha, beta, and/or photon emissions. There are many different kinds of counting instruments used to measure these emissions. Examples include:

- Alpha
 - Silicon surface barrier
 - Gas-flow proportional
- Beta
 - Gas-flow proportional
 - Liquid scintillation
- Photon
 - Gamma spectrometers (high purity germanium [HPGe] or lithium drifted germanium [GeLi] detector systems)

- Low-energy (X-ray) spectrometers.

These detector systems are used in support of a variety of analytical needs ranging from screening to isotope-specific identification and quantification.

Four main counting equipment categories are described in Table 4-1 through Table 4-4:

- Alpha and beta analysis using gas-flow proportional counting
- Gamma spectrometry
- Alpha spectrometry
- Beta spectrometry using liquid scintillation counting.

Other counting systems are available to radiochemists. While the calibration concepts described herein are also typically applicable to these other systems, use of alternate counting systems will require acceptance by the client. Specific criteria and requirements will be established on a client-specific basis.

Calibration procedures and frequency shall be established by the laboratory and shall consider the manufacturer's recommendations and the requirements specified in this section. Manufacturer recommendations may include the number of standards employed, standard (activity) levels, energy ranges, voltages, count times, reagents, or other parameters. In addition, the American National Standards Institute (ANSI) Standards ANSI N42.14, *Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radionuclides*, ANSI N42.15, *American National Standard Check Sources for the Verification of Liquid-Scintillation Counting Systems*, ANSI N42.25, *American National Standard Calibration and Usage of Alpha/Beta Proportional Counters*, and the American Society for Testing and Materials (ASTM) International Standard ASTM D7282-06, *Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements*, provide guidance for the calibration and operation of radioanalytical detector systems.

There are several fundamental aspects to calibration of counting equipment, including:

- Energy of emitted radiation
- Isotope activity
- Sample geometry
- Attenuation
- Interferences.

Table 4-1. Minimum Requirements of Calibration, Background, and Counter Control for Alpha and Beta Counting.

Calibration Requirements	Calibration Parameters and Standards ^a	Criteria	Corrective Actions	Frequency
Calibration	<p>Plateau checks as applicable</p> <ul style="list-style-type: none"> Count one standard over a range of voltage in increments <p>Crosstalk or sensitivity^b as applicable</p> <ul style="list-style-type: none"> Measure α count rate from a β source, and β count rate from an α source <p>Counting efficiency to calculate activity in sample</p> <ul style="list-style-type: none"> Count at one known level for each counting geometry at the applicable energy range <p>Weight of solids^c to calculate sample activity when mass loading occurs</p>	<p>Plot voltage versus counting activity to estimate proper operating voltages for α and/or β counting.</p> <p>Crosstalk of α in β: less than 10%.</p> <p>Crosstalk or sensitivity of β in α: less than 1%.</p> <p>Counting error $\leq 1\%$.</p> <p>Establish a curve for efficiency versus mass loading.</p>	<p>Set instrument at plateau voltage.</p> <p>Investigate the system if crosstalk criteria fail.</p> <p>Investigate the system.</p>	<p>Initial start-up, after repair, maintenance, or configuration changes if control of system cannot be re-established or demonstrated</p>
Background counting	Count detector background. Use contamination-free clean planchet.	Establish a background count rate value for total α and total β . ^d	As needed to meet DQOs.	One per day as the system is used or per batch
Counter control or control standard	Use a reliable source	Control limits: three sigma or $\pm 3\%$, whichever is greater.	Investigate. Recalibrate, if necessary.	One per day as the system is used or per batch

^a See Section 4.4.1 for calibration standards requirements, as applicable for the technique used.

^b When crosstalk has an impact on data reduction.

^c When mass loading is applicable.

^d At a minimum, the most recent background and its error obtained from the counting system should be used for background subtraction. More thorough means (e.g., 10-point running average background) for determining the appropriate background rate and its error may be appropriate for particular situations, and their uses shall be left to the discretion of the radiochemist.

Table 4-2. Minimum Requirements of Calibration, Background, and Counter Control for Gamma Spectrometry.

Calibration Requirements	Calibration Parameters and Standards ^a	Criteria	Corrective Actions	Frequency
Calibration	Detector energy calibration	No specific criteria, depending on total channel and span energy range of nuclides of interests.	Not applicable (N/A)	Initial start-up, after repair, maintenance, or configuration changes if control of system cannot be re-established or demonstrated
	Counting efficiency ^b Matrix- and geometry-specific	Span energy range of nuclides of interests.	N/A	
Background	Count detector background to establish background level	Represents the background for the time when the sample is counted. ^c	As needed to meet DQOs.	Minimum of every other week, after detector maintenance, configuration changes or after analytical run if it is longer
Counter control or control standard	Multi-energy source covering the general energy calibration range	Control limits: three sigma or $\pm 3\%$, whichever is greater. ^b System attributes such as count rate, energy calibration, and/or energy resolution (full width half maximum [FWHM]) for control peaks should be monitored.	Readjust if kev/channel drift occurs. Investigate. Recalibrate if necessary.	One per week or after analytical run if it is longer

^a See Section 4.4.1 for calibration standards requirements.

^b Only where counting efficiency is an analytical requirement.

^c The purpose is to confirm or establish current background and to test instrument contamination.

Table 4-3. Minimum Requirements of Calibration, Background, and Counter Control for Alpha Spectrometry.

Calibration Requirements	Calibration Parameters and Standards ^a	Criteria	Corrective Actions	Frequency
Calibration	Energy calibration	Use at least two alpha isotopes with resolvable energies. ^b	N/A	Initial start-up, after repair, maintenance, or configuration changes if control of system cannot be re-established or demonstrated
	Counting efficiency ^b Matrix- and geometry-specific	Use at least one recognized alpha source.	N/A	
Background	Count detector background to establish background level	Represents the background for the time when the sample is counted. ^c	As needed to meet DQOs.	At a minimum of every 4 weeks or after analytical run if it is longer
Counter control or control standard	At least two isotopes	Monitor peak location and resolution and efficiency (where counting efficiency is an analytical requirement). Control limits: three sigma or $\pm 3\%$, whichever is greater. ^b	Readjust if kev/channel drift occurs. Investigate. Recalibrate if necessary.	One per week or after analytical run if it is longer

^a See Section 4.4.1 for calibration standards requirements.

^b Only where counting efficiency is an analytical requirement. The counting efficiency for alpha spectrometers is independent of alpha energy. The counting efficiency need not be directly determined for a detector if the analyte is determined relative to an appropriate recognized-traceable internal tracer. The alpha energy peak used for calibration shall be resolvable from other peaks in the spectrum or use a peak fitting correction if integration is affected by tailing. Equally acceptable, the counting efficiency may be determined for the system and factored into the sample activity determination as long as the basis for the efficiency determination remains constant with the samples (i.e., reproducible counting geometries). At a minimum, one recognized alpha source is used to determine the detector counting efficiency.

^c The purpose is to confirm or establish current background and to test instrument contamination. At a minimum, the most recent background and its error obtained from the counting system should be used for background subtraction. More thorough means (e.g., 10-point running average background) for determining the appropriate background rate and its error may be appropriate for particular situations and their uses shall be left to the discretion of the radiochemist.

Table 4-4. Minimum Requirements of Calibration, Background, and Counter Control for Beta Spectrometry and Kinetic Phosphorescence. (2 sheets)

Calibration Requirements	Calibration Parameters and Standards ^a	Criteria	Corrective Action	Frequency
Calibration	External (instrumental) standardization	N/A	N/A	Initial start-up, after repair, maintenance, or configuration changes if control of system cannot be re-established or demonstrated
Method calibration (determining quench)	1. Quench curve ^b 2. Internal standard	Used for establishing quench level in the sample and to determine specific counting efficiency.	Investigate the system.	If matrix or cocktail changes or if control of system cannot be re-established or demonstrated. Verify after detector maintenance Add to each sample type
Counter control background	Count system background	Used to examine instrumental contamination. Not used for sample background subtraction.	Investigate the system.	One per day when the system is used
Blank	Use similar matrix of the sample Use for calculation	Used to determine matrix-specific background count rate as sample background subtraction.	Investigate the system.	One per day when the system is used
Counter control or control standard	Analyte specific if applicable reliable source (e.g., vendor-supplied sources)	Control limits: Three sigma or $\pm 3\%$, whichever is greater	Investigate. Recalibrate if necessary.	One per day when the system is used
Alternate calibration: batch approach ^c	Minimum two matrix-matched standards and blanks	Counting efficiency control limits: three sigma or $\pm 5\%$, whichever is greater.	Investigate.	Count blank and standard at beginning and end of run based on matrix type

Table 4-4. Minimum Requirements of Calibration, Background, and Counter Control for Beta Spectrometry and Kinetic Phosphorescence. (2 sheets)

Calibration Requirements	Calibration Parameters and Standards ^a	Criteria	Corrective Action	Frequency
Kinetic Phosphorescence				
Calibration	Minimum of three standards. (With one near the estimated quantitation limit [EQL].)	Calibration curve goes through zero and meet coefficient of correlation >0.99. Confirm acceptability using calibration verification within $\pm 10\%$ of true value after calibration, every 10 samples, and at the end of the run.	Investigate. Correct. Recalibrate as required.	Before each new analytical run.
Instrument blank	Monitor carry over.	<MDC	Investigate. Correct (e.g., clean or replace the cell).	Before each new analytical run, every ten sample, and at the end of the run.

^a See Section 4.4.1 for calibration standard requirements.

^b If applicable.

^c This is an alternate calibration. If this approach is used, the above requirements do not apply.

All of these fundamental aspects must be known in order to effect an appropriate and accurate calibration regardless of the counting instrumentation being calibrated. The reference source for the isotope-specific energy emission shall be documented and available for review.

The isotope(s) used in calibration shall have relevance to the emission type and energy of the analyte to be determined. Ideally, detectors should be calibrated using pure materials of the same isotopes as might be encountered in samples, since the efficiency is a function of the radiation energy. For example, a ⁹⁹Tc standard is the optimum choice for calibrating a scintillation counter used for ⁹⁹Tc analysis; ¹⁴C is acceptable for the liquid scintillation counter calibration for ⁷⁹Se as there is no standard source of ⁷⁹Se available and the β^- energies are comparable.

The isotope activity in the calibration standard shall provide sufficient counts such that random counting statistics and background contributions are not significant. This can be managed by adjusting the isotope activity and the counting time of the standard. However, the source shall not be so radioactive as to cause (1) pulse pileups, (2) dead time that is significantly different from that to be expected from routine samples, or (3) gain shift in the case of pulse height analyzer systems. Any potential impacts to the calibration from other isotopes in the calibration standards shall be assessed and documented.

Calibration of photon detectors can be effected in one of two ways, depending on the analytical need. Generally, gamma detectors are calibrated with multiple isotopes spanning the range of gamma energies identified by the DQRs. The calibration curve generated shall be evaluated for smoothness of fit of the gamma energy to the counting efficiency. Gamma calibration curves shall be linear at higher energies (varies by detector and matrix) when plotted on a log-log scale. Gamma detectors may also be useful for single isotope determinations in which case a single point calibration may be used. An example of this is a ^{85}Sr calibration for determining Sr radiochemical yields using a ^{85}Sr tracer.

Sample geometry is critical to detector calibrations. The geometry used for calibration must be reproducible for samples. Geometry includes sample shape/size, density, homogeneity, and distance from the detector. Alteration of any one or more of these factors will affect the detector counting efficiency and thus the instrument response. Software tools for geometry corrections are typically part of the software associated with gamma counting systems. The use and application of these tools is dependent upon the cognizant scientist. Software used for geometry corrections is subject to the verification and documentation requirements in Volume 1, Section 7.0. Whenever software geometry corrections are applied, the client shall be notified; to either concur with the approach or agree on an alternative.

Multiple calibration curves are often generated during instrument calibration(s) from multiple standard preparations (e.g., attenuation curves for multiple detectors, efficiency curves for multiple geometries). The data for these calibrations shall be evaluated for consistency.

Attenuation of radiation affects all detector types. Attenuation is attributable to a variety of conditions, including mass loading on planchets for α/β counting, sample density in the case of photon counting, and quenching effects in the case of liquid scintillation. Where the attenuation is not fundamentally corrected in the calibration (e.g., constant density/matrix between samples and standards) an attenuation calibration will need to be performed. Examples of this include developing quench curves for liquid scintillation and mass calibration curves for α/β counting. Attenuation calibrations shall encompass working ranges (e.g., mass on planchets for α/β counting) specified by the procedures and shall contain sufficient data points to allow statistically significant curve fitting.

Interferences are often a fundamental problem in counting and can occur during calibration and analysis. Examples of interferences are α/β cross-talk for gas proportional counting, coincident summing, dead time or pulse pileup of gamma spectral photons, and peak tailing in alpha spectrometry. Potential interferences shall be evaluated. Processes to control or manage interferences shall be documented as part of the calibration and analysis procedures. Software tools for interference corrections and or peak tailing are typically part of the software associated with gamma and alpha spectral counting systems. The use and application of these tools is dependent upon the cognizant scientist. Software used for interference corrections is subject to the verification and documentation requirements in Volume 1, Section 7.0.

Radiation detection instruments are generally very stable, and instrument response can remain constant over a period of years. Calibration standard preparation is often a lengthy process along

with the instrument calibration. A detector calibration may take days and remain valid for years. Counter control measurements (Section 6.3.3) are performed periodically to confirm instrument stability.

4.4.2 Inorganic Analysis

Instrument calibration should be performed based on the manufacturer's recommendations and should establish a working response range. Calibration requirements such as frequency, criteria, and corrective action for inorganic analysis are provided in Table 4-5. The accuracy of the calibration shall be confirmed by performing an ICV immediately after calibration (see Section 6.5.2). The performance of an instrument measurement system during an analytical run shall be verified by a CCV (see Section 6.5.3).

The laboratory is required to take corrective action when measurement systems fail calibration QC criteria, as demonstrated by the procedures discussed in Section 6.0.

Table 4-5. Minimum Calibration Requirements for Inorganic Analyses. (3 sheets)

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
ICP spectrometer	Profile (optical alignment) Blank and one concentration per analyte of interest	Before each new analytical run. ^a	Meet manufacturer's recommendations for centroid and FWHM. Confirm acceptability using ICV. ^b	Investigate. Correct if necessary. Investigate. Correct. Recalibrate as required.
Inductively coupled plasma/mass spectrometer (ICP/MS)	Tune Check mass calibration Calibrate using at least a blank and one standard according to manufacturer's recommendations	Analyze four times at the beginning of each analytical run. Before each analytical sequence.	Relative standard deviation (RSD) $\leq 5\%$. Mass calibration must be less than 0.1 amu of actual value. Resolution must be less than 0.9 amu full width at 10% peak height. Calibration verification within $\pm 10\%$ of true value.	Investigate. Correct. Adjust mass calibration to correct value. Investigate. Correct. Recalibrate.
Graphite furnace atomic absorption and flame atomic absorption	Blank and minimum of three concentrations that bracket instrument working range	Before each new analytical run. ^a	Meet coefficient correlation of >0.995 . Confirm acceptability using ICV. ^b	Investigate. Correct. Recalibrate as required.

Table 4-5. Minimum Calibration Requirements for Inorganic Analyses. (3 sheets)

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
Hydride atomic absorption (arsenic and selenium)	Blank and five standards	Before each new analytical run. ^a	Meet coefficient correlation of >0.995. Confirm acceptability using ICV. ^b	Investigate. Correct. Recalibrate as required.
Cold vapor (manual atomic absorption) Automated	Blank and three concentrations that bracket 5 µg/L working range, or blank and four concentrations that bracket 10 µg/L working range	Before each new analytical run. ^a	Meet coefficient correlation of >0.995. Confirm acceptability using ICV. ^b	Investigate. Correct. Recalibrate as required.
	Blank and four standards (linear response)	Before each new analytical run. ^a	Meet coefficient correlation of >0.995.	Investigate. Correct. Recalibrate as required.
	Blank and eight standards (non-linear response)		Confirm acceptability using ICV. ^b	
Cyanide-manual and semiautomated spectro-photometer	Blank and three concentrations (undistilled) that bracket working range	Before each new analytical run ^a with the following exception: for dedicated instruments, when six concentrations are used in the calibration, the calibration is valid as long as calibration verification acceptability is demonstrated or for up to 90 days.	Meet coefficient correlation of >0.995. Confirm acceptability using ICV. ^b The distilled standard requirement is covered by the LCS, Table 6-3.	Investigate. Correct. Recalibrate.
Ion chromatography (IC)	Blank and three concentrations that define working range	When calibration verification fails	Meet coefficient of correlation >0.995. Confirm acceptability using ICV. ^b	Investigate. Correct. Recalibrate as required.

Table 4-5. Minimum Calibration Requirements for Inorganic Analyses. (3 sheets)

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
pH	Two-point, calibration; 3 pH units or more apart from calibration range representative of sample results For corrosivity characterization, one buffer should be a pH of 2 for acidic wastes and a pH of 12 for caustic wastes	Before each new analytical run. ^a	For dial or slope calibration, analysis of calibration standards must measure within 0.05 pH units of true value. A calibration verification standard within 0.1 pH units of true value confirms acceptability of calibration.	Investigate. Correct. Recalibrate as required.
Ion selective electrode				
Working curve technique	Minimum of three standards with one near the EQL, to define the working range	Before each new analytical run. ^a	Calibration verification within $\pm 10\%$ of true value.	Investigate. Correct. Recalibrate as required.
Standard-addition technique	Follow manufacturer's method-specific recommendations	All samples, standards, and blanks.	Calibration verification within ± 3 standard deviations of the historical mean.	
Titrimetric	N/A	N/A	Standardize titrant(s) before use. Evaluate results based on QC presented in Sections 6.5.2 and 6.5.3.	N/A
Colorimetric	Blank and minimum of three standards, with one near the EQL, to define the working range	Before each new analytical run. ^a	Calibration verification within $\pm 10\%$ of true value.	Investigate. Correct. Recalibrate as required.

^a Analytical run is defined as a sequence of analyses within a continuous time period (see Section 6.5.1).

^b See Section 6.5.2 for ICV acceptance criteria.

4.4.3 Organic Analysis

Instrument calibration shall be performed to establish a working response range. Calibration requirements for frequency, criteria, and corrective action for organic analysis are provided in Table 4-6, Table 4-7, and Table 4-8. The calibration accuracy shall be confirmed by performing an ICV immediately after calibration (see Section 6.7.2). The performance of an instrument measurement system during an analytical sequence shall be verified by a CCV (see Section 6.7.3). When the concentration of any calibrated target constituent in a sample extract (or purged sample analyzed for volatile organic compounds [VOCs]) exhibits an instrument response that exceeds the highest standard concentration in the initial calibration, the sample extract must be diluted (or sample size for VOC analysis reduced) to ensure the final concentration for the applicable constituent is determined using an analysis with a concentration between the lowest and highest concentrations of the standards used in the initial calibration.

The manufacturer's specifications for tuning the gas chromatograph (GC)/mass spectrometer system shall be met before calibration. All systems incorporating a GC should have the retention time window specifications evaluated each time the GC system parameters are changed and whenever a new column is installed.

Continuing calibration should be verified routinely or before running samples. The laboratory is required to take corrective action when organic measurement systems fail calibration as demonstrated by the procedures discussed in Section 6.0.

Sufficient raw data records must be retained to permit reconstruction of the continuing instrument calibration verification (e.g., test method, instrument, analysis date, each analyte name, concentration and response, calibration curve or response factor [RF], or unique equations or coefficients used to convert instrument responses into concentrations). CCV records must explicitly connect the continuing verification data to the initial instrument calibration.

**Table 4-6. Minimum Requirements for Gas Chromatograph/
 Mass Spectrometer Systems. (3 sheets)**

Calibration	Calibration Standards	Acceptance Criteria	Corrective Action	Frequency
Tuning instrument performance check	Specific tuning compound, either purge or inject.	Shall meet regulatory criteria if applicable, otherwise meet manufacturer's recommendation.	Re-tune or repair as necessary.	12 hours

**Table 4-6. Minimum Requirements for Gas Chromatograph/
Mass Spectrometer Systems. (3 sheets)**

Calibration	Calibration Standards	Acceptance Criteria	Corrective Action	Frequency
Calibration (initial) ^a	The numbers of concentrations of analytes of interest are based on RCRA, CERCLA, or others ^c (see CCV). All compounds used are specified by laboratory and client agreement.	Validate calibration curve to meet appropriate regulatory or other ^c criteria for RF and percent relative standard deviation.	N/A	Upon failure of ICV or CCV
System performance check compounds ^b when appropriate	Compounds used are based on RCRA or others. ^c	Meet appropriate regulatory or other ^c criteria.	Investigate the system or re-run.	Run with every initial calibration and CCV
Calibration check compounds ^b when appropriate	Compounds used are based on RCRA or others. ^c	Meet appropriate regulatory or other ^c criteria.	Investigate the system or re-run.	Run with every calibration and CCV to ensure calibration and CCV is within control
CCV	Mid-range calibration standard and internal standards. All compounds used are required by laboratory and client agreement.	Validate calibration curve to meet regulatory or other ^c criteria for RF, retention time, and percent difference between initial and continuing calibration.	Investigate the system and initiate corrective action.	12 hours
Internal standards ^d	Compounds used are based on RCRA or CERCLA.	Meet appropriate regulatory criteria.	Investigate the system or re-run calibration check compounds, and re-run any sample with internal standard not meeting criteria.	Included in every standard solution, blank, and sample

**Table 4-6. Minimum Requirements for Gas Chromatograph/
Mass Spectrometer Systems. (3 sheets)**

Calibration	Calibration Standards	Acceptance Criteria	Corrective Action	Frequency
Surrogates	Similar behavior to analyte of interest. When performing an established method, all requirements shall be followed, unless client requests otherwise.	Meet appropriate regulatory or other ^c criteria.	N/A	Included in every sample, calibration, ICV, and CCV
Instrument/ method blank	Analyte free water, surrogates, and internal standard.	All analytes less than detection limits, with the exceptions based on RCRA, CERCLA, or other ^c criteria.	Correct problem. Re-run any samples that are affected.	Run one blank before sample analysis

^a RF is equivalent to relative response factor for Contract Laboratory Program.

^b Nomenclature is based on EPA SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*.

^c Other criteria that are required by either a DQO, laboratory and client agreements, or regulator approval.

^d Internal standard shall be used. Internal standard-specific compounds are suggested and not mandatory. If other compounds are chosen, they shall cover the entire retention time range, not interfere with analytes, and not degrade. The primary ion from the appropriate internal standard compound is used to ratio to the ion from the analyte of interest.

**Table 4-7. Minimum Requirements of Calibration and Calibration Verification
for Gas Chromatograph System. (2 sheets)**

Calibration Requirements	Compounds	Criteria	Corrective Actions	Frequency
Calibration: external standard approach	Minimum three concentrations per analyte of interest, with one near the MDL to define the working range of the detector. ^a Target compounds ^b or analytes per laboratory and client agreement. Surrogates.	Calibration factor (CF) and percent RSD shall be calculated for each compound. Validate the calibration curve to meet regulatory or other ^c criteria for percent RSD of CF.	Investigate the system or re-run if necessary.	After major maintenance or upon failure of CCV

Table 4-7. Minimum Requirements of Calibration and Calibration Verification for Gas Chromatograph System. (2 sheets)

Calibration Requirements	Compounds	Criteria	Corrective Actions	Frequency
Alternate calibration: internal standard approach	<p>Minimum three concentrations per analyte of interest with one near the MDL to define the working range of the detector.^a</p> <p>Target compounds^b or analytes per laboratory and client agreement.</p> <p>Surrogates.</p> <p>Add internal standard to all standards and samples.</p>	<p>RF and percent RSD shall be calculated for each compound.</p> <p>If an RF value is constant over the working range, validate the calibration curve and use it for calculations.</p>	Investigate the system or re-run if necessary.	After major maintenance or failure of CCV
CCV	Using one or more calibration standards.	<p>Working calibration curve verified by the measurements of one or more calibration standards.</p> <p>Meet percent difference of CF criteria between initial and continuing calibration based on RCRA, CERCLA, or other^c criteria.</p>	Investigate the system or re-run a new calibration curve.	Daily, when used, and before analytical run

^a For RCRA or CERCLA type of work, either EPA SW-846 or Contract Laboratory Protocol shall be used.

^b Select one or more internal standards similar in analytical behavior to the compounds of interest.

^c Other criteria are required by either a DQO, laboratory and client agreements, or regulator approval.

Table 4-8. Minimum Calibration Requirements for Total Organic Carbon, Total Inorganic Carbon, and Total Carbon Analysis Using Different Instruments.

Instruments	Calibration	Frequency	Acceptance Criteria	Corrective Action
Combustion-infrared method Persulfate-ultraviolet oxidation Wet-oxidation method	According to manufacturer's recommendation Blank and sufficient standards should be used that encompasses the expected concentration	Before each new analytical run ^a or every 15 samples	Follow manufacturer's recommendations	Investigate. Correct if necessary. Recalibrate as required.
Coulometric method	Initial calibration performed by manufacturer	Confirm acceptability using performance check	±3 standard deviation of historical mean of the performance check	Investigate. Correct if necessary.

^a Analytical run is defined as a sequence of analyses within a continuous time period (see Section 6.5.1).

4.4.4 Physical Testing

Minimum calibration requirements for several physical tests are presented in Table 4-9.

Table 4-9. Minimum Calibration Requirements for Thermogravimetric Analysis, Differential Thermal Analysis/Thermal Gravimetry, and Differential Scanning Calorimetry.

Technique	Calibration Requirements	Criteria	Frequency	Corrective Action
Thermogravimetric analysis	Initial calibration performed by manufacturer	Confirm acceptability using performance check (temperature and balance checks)	Upon failure of performance check	Recalibrate when performance cannot be re-established
Differential thermal analysis/thermal gravimetry	Initial calibration performed by manufacturer	Confirm acceptability using performance check (temperature and balance checks)	Upon failure of performance check	Recalibrate when performance cannot be re-established
Differential scanning calorimetry	Initial calibration performed by manufacturer	Confirm acceptability using performance check (temperature and enthalpy checks)	Upon failure of performance check	Recalibrate when performance cannot be re-established

5.0 DATA COLLECTION, REDUCTION, AND REPORTING

Data collecting and reporting processes include proper sampling, correct chain-of-custody, collection of raw data, data reduction and calculations, interpretations, reporting conventions, review, confirmation, and transferring results to a final form for reporting. All resulting records shall be maintained in a manner to safeguard the data and meet regulatory requirements as described in Volume 1, Section 6.0.

5.1 DATA COLLECTION

Raw data includes all parameters used to calculate a final reportable result. Raw data can be generated by manual and/or electronic means. Manual data generation shall be collected and recorded by the analyst according to applicable procedures. Many analytical instruments are interfaced with computers and/or integrators and are able to generate or reduce the raw data into reportable results.

Observations, records, and results recorded by the laboratory shall be on pre-printed forms, electronic media, or entered into permanent laboratory logbooks. Entries into logbooks shall be made in a manner such that they can be easily read, understood, and reproduced with a standard photocopier.

When notebooks/logbooks are required they shall be permanently bound or have a means to eliminate page removal/replacement (e.g., tamper seals), loose-leaf binders shall not be used. Notebooks/logbooks shall have:

- A unique identifier clearly displayed
- Sequentially-numbered pages
- Entries are made in a permanent fashion and corrections are made without obliterating the original data.
- Entries are dated and signed by the person responsible for performing the activity at the time the activity is performed.

Entries are in chronological order. When no more entries are to be made on a page, unused portions of the page will be struck out, signed/initialed, and dated.

Electronic notebooks are permitted and shall meet the same requirements for change protection and controls as hand-written hardcopy notebooks.

Raw data output shall be retained as a part of the records (see Volume 1, Section 6.0). Sufficient raw data should be retained to allow reconstruction of the analytical run. Information on date of sample collection, sample preparation, and analysis run; sample identification numbers; analyst

or instrument operator; instrument identification and operating parameters; type of analysis; and procedure number, including revision number, shall be traceable to the raw data output.

5.2 DATA REDUCTION

Data reduction is defined as the mathematical operations applied to the raw data to produce a final reportable result. Data resulting from analyzing samples shall be reduced according to procedures that address the concepts discussed in this section. Data reduction includes activities that convert instrument and computer responses into reportable results. These activities may involve calculations, changes to the units or the data values, and statistical and mathematical analysis.

Computer programs or spreadsheets used for data reduction shall be verified before reporting data to ensure calculation and data manipulation programs perform properly.

The following practices shall be in place to ensure accuracy of data entry, proper calculation, and appropriate data reduction:

- Verify that all readings or output are accurate.
- Ensure proper error correction or data change (i.e., one line through, dated, initialed, and explained as appropriate).
- Select appropriate formulas for calculating final results, correct for appropriate backgrounds and/or interference (e.g., Compton effects for gamma energy analysis and inter-element correction for ICP spectrometer), and document calculations and results.
- Verify that data are accurately transcribed into notebooks, forms/benchesheets, or spreadsheets.

5.2.1 Significant Figures

The number of significant figures reported is a function of the limits of the particular analysis method. Basic rules for significant figures and for calculating values and retaining the number of significant figures shall be based upon an authoritative source or accepted standard such as the ASTM E-29, *Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications*.

Reported values should contain only the appropriate number of significant figures. Recognizing that vendor-supplied software may not meet the general rules for significant figures, the laboratory should work with the client to determine the best way to report results, based on the project needs.

5.2.2 Rounding-Off Methods

When a figure is to be rounded to fewer digits than the total number available, the rounding-off procedure shall be based upon an authoritative source or accepted standard such as that described in ASTM E-29. A brief interpretation of the ASTM E-29 procedure follows:

- When the first digit discarded is less than five, the last digit retained should not be changed.
- When the first digit discarded is greater than five, the last figure retained should be increased by one.
- When the first digit discarded is exactly five, followed only by zeros, the last digit retained should be rounded upward if it is an odd number, but no adjustment made if it is an even number.

5.2.3 Data Review

Data review refers to the process of determining if data conforms to specified requirements. A system shall be in place in accordance with laboratory-established procedures to review data before data reports are issued. Errors detected in the review process shall be referred to the analyst for corrective action (see Volume 1, Section 5.0). The data review process shall be documented with the records retained and available for review. The data review process shall incorporate the following elements and those discussed in Section 8.0:

- Data shall be reviewed according to laboratory procedures to verify that calculations are correct and to detect transcription errors.
- Sample data review shall include verification of sample identification number, analyst, and date of analysis.
- Data shall be reviewed against applicable QC and method criteria to verify that the preparative and/or analytical system is performing acceptably (see Section 5.0 for details). If QC samples did not meet QC criteria, data within the batch shall be evaluated to determine if there were any adverse effects on the data; the sample shall be re-prepared and/or rerun, or the data shall be reported with qualification(s), which will be detailed in the narrative as appropriate to the condition.
- Data review shall include all quality related steps in the analytical process, (e.g., sample preparation, dilution calculations, chromatography evaluation, spectral interpretations).
- Data shall be reviewed against project-specific criteria as established in the laboratory-client agreements. This review includes chain-of-custody, holding times, unique QC specifications, required detection limits, completeness (i.e., requested analytes reported), TICs, report format (hardcopy and electronic), turnaround time, anomalies and nonconformances, as applicable. All efforts shall be made to meet the client requirements. Identified issues shall be documented and communicated to the client.

- Random checks shall be performed to verify data entry, calculations, and QC criteria.
- For counting-based radioanalytical analysis, negative results below -3 sigma (combined standard uncertainty) are evaluated. If the cause is random, the problem is addressed in the case narrative. If the cause is systematic, the problem is corrected and the affected sample(s) shall be re-prepared and/or rerun if sufficient sample material remains, unless client-specific requirements/specifications dictate otherwise. The client shall be notified prior to such actions when additional costs will be incurred. When client requirements/specifications cannot be met, the client shall be notified; results shall either be accepted or new work scope agreed on.

5.3 DATA REPORTING

The analytical information reported should include the measured parameters, the details of analysis, the reported data values, and associated data qualifiers in accordance with client requirements. Section 7.5 contains details on defining detect/non-detect status for analyses.

Inorganic or organic results shall be reported as numeric values with appropriate data qualifiers

Radiochemical results shall be reported based on calculated concentration or activity values (whether negative, positive, or zero) using the appropriate blank for each nuclide. The measured activity or concentration should be reported with estimates of both counting uncertainty and total propagated uncertainty. The MDC should not be reported to the client *in lieu* of low-level measurements for non-detected results.

5.3.1 Data Reporting Documentation

The reporting documentation shall include the following information:

- Laboratory name and address.
- Sample information, including unique laboratory identifier cross-referenced to client identification, sample collection date and time (when holding times apply or upon request), date of sample receipt, and date(s) of sample preparation and analysis.
- Analytical units and results, reported with an appropriate number of significant figures and associated uncertainty for radiochemical results.
- Detection limits.
- Method references.
- Identification of any amended test results.
- Signature and title of person accepting responsibility for the report contents.

- Date of issue.
- Identification of subcontracted results if applicable.
- Appropriate QC results (correlation with sample batch shall be traceable and documented).
- Appropriate data qualifiers with definitions and a narrative on the quality of the results, if applicable.
- Additional data reporting, (e.g., the percent of moisture/solid or correction for equivalent dry weight) as appropriate.

5.3.2 Immediate Reporting

When applicable to a client's needs, an immediate data reporting system shall be established between the laboratory and the client to address an emergency situation. The type of information, level of approval, data reporting format, and means of delivery shall be discussed and agreed upon between the laboratory and the client. The emergency situation may include but is not limited to screening activities for safety issues, critical analytes, or limiting sample amount.

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6.0 QUALITY CONTROL

QC is defined as the overall system of activities that provides checks and balances to the quality of a product or service. QC data is evaluated against client requirements to measure how well the data meets the client's needs. The goal is to provide data of known quality that is adequate for the intended purpose. QC data allows the laboratory and the client to measure the degree of conformance against the requirements.

To assess the precision, accuracy, and sensitivity of a reported result, QC checks are incorporated throughout the data collection process (e.g., sample preparation/separation, analysis, reporting) to provide a measurement tool for evaluating the effectiveness of the process. QC checks provide information with regard to performance of the measurement system, and the environmental and matrix-related impacts on the measurement system. The information gained from evaluating QC performance can then be used to implement corrective actions or improve processes.

The QC requirements for each of the three major types of analysis (i.e., radiochemical, inorganic, and organic) conducted in support of Hanford environmental programs are discussed separately. Physical testing QC requirements are also provided for several test parameters (see Section 6.8). Each of the fields of chemistry is further subdivided into two parts: preparation/separation QC and measurement/counting QC. The text and the accompanying tables provide the detailed QC requirements for each topic. Basic QC operations, applicable to all analytical disciplines, are presented in Section 6.1. Basic QC operations consist of controlling the quality of solvents, standards, reagents, and gases used in the laboratory.

Where a Hanford Site activity requires using a specific regulatory method (e.g., permits, National Pollutant Discharge Elimination System), and the regulatory method is in conflict with HASQARD, the calibration and QC requirements in the regulatory method shall take precedence over Sections 4.0 and 6.0 in Volume 4 of HASQARD. All other sections of HASQARD would apply.

The QC requirements presented are designed to enable both the laboratory and the client to ascertain the quality of the data produced. These QC checks provide information on the precision, accuracy, sensitivity, and overall reliability of the reported results. Each laboratory is required to implement and meet the basic QC requirements outlined in this section. However, client DQRs shall always be used to determine if sample results can be reported and shall take precedence over these criteria. In certain instances, a result may fall outside of the specifications in this section but still meet client needs. In such cases, the results would be considered acceptable for reporting. Reported results shall be traceable to the QC performed with those results.

6.1 GENERAL LABORATORY QUALITY CONTROL

The QC described in this section represents the basic laboratory systems associated with analytical operations and applies to radiochemical, inorganic, and organic analytical procedures. The use of substandard reagents, standards, materials, and equipment can result in less reliable or

unreliable data. Each laboratory shall have a mechanism in place for demonstrating control over those sources that affect the accuracy, precision, and sensitivity of reported results. The minimum requirement would consist of monitoring analytical and preparative blanks for contamination from these sources. If contamination is discovered, the laboratory shall investigate and have a process in place to identify and eliminate the source and determine which samples may have been impacted. When a contamination source is identified, the laboratory shall implement measures to prevent recurrence.

If repeated QC measurements exceed control limits (e.g., two consecutive or if noted as a trend), the laboratory shall determine the cause for the nonconformance and take appropriate corrective actions prior to analysis of further samples. All data generated since the last acceptable check shall be considered suspect and investigated. Where sufficient sample remains, all affected samples shall be re-prepared and analyzed, unless client-specific DQRs dictate otherwise. When client DQRs cannot be met, the client shall be notified for resolution.

The methodologies employed to prepare and analyze client samples shall be the same as those performed upon laboratory QC samples and consistent for a given analytical batch. Preparation procedures shall be established by the laboratory and shall consider the manufacturer's recommendations or requirements (e.g., specific sample vial configuration/composition, reagent to analyte ratios, special reagent handling, etc.) where applicable.

6.1.1 Distilled or Deionized Water

High-purity water is generally defined as water that has been distilled or deionized, or both, so that it will have conductivity less than 1.0 $\mu\text{S}/\text{cm}$ (greater than 1.0 megaohm-cm resistivity). Each laboratory is responsible for ensuring that the water used for data collection activities is of sufficient quality for the operation performed. Water quality is regularly monitored via preparative and analytical blank performance.

6.1.2 Compressed Gases

Each laboratory shall monitor the quality of gases used in the laboratory to ensure that they are adequate for the operation being performed. At a minimum, this shall consist of monitoring system performance (e.g., for contribution to background and/or blanks from impurities).

6.1.3 Standards

The acceptability of standards used in the preparation and analysis of client samples shall be defined and verified. Each laboratory shall document its criteria and method(s) of verification. See Section 4.3 for guidance on standard selection, use, and verification.

6.1.4 Reagents

Each laboratory is responsible for ensuring that reagents used for data collection activities are of sufficient quality for the operation performed. The acceptability of quality affecting reagents shall be assured by checking reagent lots prior to use (e.g., checking clean-up reagents such as

Florisil to ensure adequate recovery of analytes and adequate exclusion of interferences) or ordering reagents with documented certification of purity. Reagent quality is regularly monitored via preparative and analytical QC performance. Supporting documentation regarding preapproval of the reagents used shall be filed in a manner that is retrievable. Purchased stock mixtures and reagents shall be labeled to indicate the date on which the mixtures/reagents were opened and the expiration date. The laboratory will either verify the concentration of titrants used in accordance with written laboratory procedures or purchase titrants with certificates of analysis.

6.1.5 Labware

Each laboratory shall purchase and use labware of sufficient quality to meet client requirements. Labware selected shall be compatible with the testing being performed.

6.1.6 Glassware Cleaning

Glassware cleaning shall be performed such that sample contamination is minimized.

6.1.7 Good Housekeeping

Each laboratory shall ensure that operations are performed in a clean and organized manner to maximize available workspace and minimize cross contamination of samples. Laboratories shall clean common sample processing equipment (e.g., grinders) between samples and maximize use of disposable sample handling equipment (e.g., spatulas, pipettes, or balance pans) to minimize cross sample contamination. To the extent it is known beforehand, analysts should process samples from expected “low” concentration to “higher” concentration.

6.2 PREPARATIVE TECHNIQUES FOR RADIOCHEMISTRY

Preparative techniques are those operations used to prepare a sample for instrumental analysis (i.e., counting). Radiochemistry generally separates preparative techniques into two types: sample preparation that prepares the sample material for the second step, and radionuclide separation (isolation). The first technique, sample preparation, modifies the original sample matrix, freeing the radionuclides for further separation prior to counting (quantitation). Examples of preparative techniques are evaporating water samples to dryness, acid leaching soils and air filters, wet ashing organic matter, fusion, and acid digestion. The second technique, separation, involves isolating specific radionuclides from other radionuclides that may interfere with accurate quantitation of the target analyte. Examples of separation techniques include ion exchange chromatography and selective solvent extraction.

In this context, separation and/or isolation techniques are preparative, if performed before counting, to facilitate accurate measurement. Simple dilution is not a sample preparation technique. Selection of a preparative technique should be based on client DQRs. See the discussion in the following subsections and Table 6-1 for frequency requirements used during preparation.

Table 6-1. Preparative Requirements for Radiochemistry Quality Control.

Quality Control Requirements	Frequency	Criteria	Corrective Action
Preparation/ method blank	One per batch	< MDC, < 2 x total propagated uncertainty (TPU), < 5% sample isotope concentration, or < 5% client required detection limit or decision level	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Blank spike (BS) ^a -or- LCS ^a	One per batch One per batch	80 to 120% or statistical ^c Vendor or statistical ^c	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative. Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Sample duplicate	One per batch	≤ 20% relative percent difference (RPD) when the two results are > 5 times the MDC or the individual uncertainties are < 20%. Or, alternately, the duplicates should agree within two standard deviations.	Evaluate. If laboratory error, re-prepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Matrix Spike (MS) ^{a,b}	One per batch	75 to 125% -or- statistical ^c	Evaluate. If laboratory error, re-prepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.

^a Nondestructive radioanalytical techniques *do not* require a MS; however, a BS or LCS is desirable.

^b The decision to perform a spike during or after preliminary preparation shall be based on sample activity levels. This spike requirement may be met using a MS, tracer, or carrier depending on client requirements and considerations discussed in Section 6.2.4.

^c Laboratory developed procedures shall either meet specifications or show statistical basis for alternative criteria. Alternative criteria are acceptable if they meet client DQRs.

6.2.1 Preparation/Separation Batch

A batch is a group of samples, of similar matrix type, prepared and/or separated at the same time. A batch shall not exceed 20 client samples. If clients do not specify project-specific QC, the laboratory may combine up to 20 samples of a similar matrix type for preparation with only one duplicate (or matrix spike duplicate [MSD]) and MS required. In the case of process testing or unique client requirements, QC elements such as a sample duplicate (or MSD) and MS may be performed for every 20 client-specific samples received. However, the preparation blank and LCS/BS requirement would apply to each batch of samples prepared at one time.

A sample or series of samples that do not require preparation or separation prior to analysis would not fall under the requirements in this section. Additionally, limited sample quantity may limit the laboratory's ability to meet the duplicate and MS requirements. In such cases, alternative approaches should be considered to demonstrate sample precision and accuracy. Unique client requirements shall be documented and agreed on by the laboratory and the client before work begins.

6.2.2 Preparation Blank or Method Blank

The sample preparation blank or method blank is used to monitor contamination resulting from the sample preparation process. The preparation blank or method blank is generally distilled or deionized water, which is subjected to the same processing as the samples, including all reagent additions. The laboratory is also free to use a matrix more closely related to the actual samples processed (i.e., clean soil, synthetic tank waste) provided the matrix is free of contamination from analytes of interest above those naturally occurring in nature.

The weight or volume of blank material used should be selected such that it will result in a reasonable approximation to that of the samples and shall be presented in the same context as the samples. In any event, the blank should be evaluated for its contribution to the sample, based on how the sample was prepared. Preparation or method blanks shall be prepared with each batch of samples processed at the same time.

Preparation or method blank acceptability shall be demonstrated as follows: (1) the blank shall be less than the estimated MDC or 2 x TPU of the associated samples, or (2) if the blank is equal to or above the estimated MDC or 2 x TPU, it shall not exceed 5 percent of the measured activity present in the associated samples, or (3) when a decision level or client required detection limit is specified, the blank shall not exceed 5 percent of the decision level or client required detection limit unless (2) above applies.

NOTE: *The laboratory must be capable of achieving an MDC less than or equal to 5 percent of the "decision level" or must negotiate an acceptable alternative.*

In those cases where preparation blank (method blank) criteria are not met, the source of error shall be investigated. If a laboratory error is identified, and where sufficient sample remains, all affected samples in the preparation batch will be re-prepared and analyzed unless client-specific DQRs dictate otherwise. The client shall be notified prior to such actions when additional costs

will be incurred. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or new work scope agreed upon.

The results of the preparation blank analysis should be reported to the client as part of routine reports. Preparation blank results are not subtracted from sample results unless client DQRs specify otherwise; in which case, the case narrative accompanying the results should state that blank subtraction was used.

6.2.3 Laboratory Control Sample or Blank Spike

A LCS or BS is used to monitor the effectiveness of the sample preparation process. The LCS is a material similar in nature to the sample being processed containing the isotope(s) of interest (e.g., standard reference material). The BS is distilled or deionized water, or other suitable substrate spiked with the isotope(s) of interest. The blank, spiked with tracer would also meet the BS requirements. A BS is normally used when an appropriate LCS is unavailable.

The decision on when and how to introduce an LCS/BS into an analytical batch may be based on the anticipated sample analyte activity or required dilution. For samples that exhibit high activity, introduction of an LCS/BS at the initiation of sample preparation is not justifiable, either because of standard material consumption or radiation dosimetry issues. Likewise, a large subsequent dilution can waste expensive standard material. Therefore, an LCS/BS may be introduced after preliminary sample preparation and dilution, but before any radiochemical separation occurs. The LCS/BS should be added as early in the analytical process as is practicable. In these cases, it is acknowledged that the LCS/BS is monitoring only the effectiveness of the separation, purification, and counting process rather than the entire sample preparation process. An LCS, if available, or BS shall be prepared with each batch of samples processed at the same time and, cognizant of the limitations discussed above, should be configured to mimic the samples in the preparation batch as much as possible.

The isotope activity(ies) in the LCS/BS shall provide sufficient counts such that random counting statistics and background contributions are not significant. However, the source shall not be so radioactive as to cause (1) pulse pileups, (2) dead time that is significantly different from that to be expected from routine samples, or (3) gain shift in the case of pulse height analyzer systems. However, LCS/BS activities should always provide results exceeding the decision or action limit.

BS control is demonstrated by target analytes being within either the preset limit of 80 to 120 percent, or within statistically determined limits when the ± 20 percent criteria cannot be reliably achieved.

LCS acceptability is demonstrated by target analytes being within established control or acceptance limits. Control limits are either provided by the vendor or statistically determined by multiple analyses over time. For the LCS, the vendor-supplied precision may affect the acceptance limits applied to the analyte.

The laboratory must ensure that each method used for a given scope of work is capable of meeting client precision and accuracy requirements or the laboratory must negotiate alternative requirements.

In those cases where LCS/BS criteria are not met, the source of error shall be investigated. If a laboratory error is identified, and where sufficient sample material remains, all samples in the preparation batch shall be re-prepared and analyzed unless client-specific DQRs or agreements dictate otherwise. In cases where an LCS/BS was introduced after initial preparation/dilution, unless total re-analysis is specifically required by the client, re-preparation/re-analysis may be started at the point the LCS/BS was introduced to the batch. In limited cases, results may be acceptable for reporting provided the laboratory can demonstrate that the client DQR was still achieved. The client shall be notified prior to re-preparation if additional costs will be incurred. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or new work scope agreed upon.

The LCS/BS results should be reported to the client. No adjustment of client sample results based on LCS recovery is made in the laboratory report.

6.2.4 Matrix or Post Spike

In general, MS is a term given to a client sample that has been spiked with the analyte(s) of interest and processed in the same manner as the sample. The MS is used to monitor method performance in a specific sample matrix. MS results are an indicator of the effect the client sample matrix has on the accuracy of measurement of the target analytes.

In radiochemistry, the MS represents the addition of a known quantity of the isotope of interest to an aliquot of sample. This spike may be added to a sample aliquot prior to any sample preparation (i.e., fusion, leaching). Alternatively, it may be elected prior to specific radiochemical manipulation (e.g., separation chemistry or evaporation onto a planchet). A spike added at this point can indicate matrix-related effects remaining after preparation, but gives no measure of the efficiency of the original preparation step. Whenever practical, other spike recovery data (i.e., inorganic recovery results from the same preparation) should be used to identify potential analyte losses.

The decision on when and how to spike a sample is based on the anticipated sample analyte activity or required dilution. Spiking additional activity into a sample that already exhibits high activity is not justifiable, either because of standard material consumption or radiation dosimetry issues. Likewise, spiking before a large dilution can waste expensive standard material. Therefore, spiking may be performed after preliminary sample preparation and dilution, but before any radiochemical separation occurs. When required, a MS shall be prepared with each batch of samples processed at the same time and, cognizant of the limitations discussed above, should be configured to mimic the samples in the preparation batch as much as possible.

The isotope activity(ies) in the MS shall provide sufficient counts such that random counting statistics and background contributions are not significant. However, the source shall not be so radioactive as to cause (1) pulse pileups, (2) dead time that is significantly different from that to

be expected from routine samples, or (3) gain shift in the case of pulse height analyzer systems. However, spike amounts should always provide results exceeding the decision or action limit.

When the analyte concentration is unknown, spiking is typically performed at one of the following levels: (1) equivalent to the threshold established by the DQO process, (2) specified by method, or (3) one to five times the MDC. Otherwise (as general guidance), the spiking should be performed at a level equivalent to one to five times that of the sample. In those instances where the analyte concentration significantly exceeds the amount of spike added in the prepared samples, the data must be further evaluated to determine if the analyte response of the spiked sample is statistically significant. If not, a re-run of the process may be required depending on client needs.

The laboratory shall evaluate MS recovery information against client DQRs. The goal is to ensure that limitations on the data, caused by the sample matrix and represented by MS performance, are adequately portrayed and discussed in the report to the client. It should be noted that client results would already be corrected for matrix and/or handling effects, if a tracer or carrier is used in place of a MS.

The criteria for selection and recovery (maximum and minimum limits) of MS materials shall be specified. Nominal recovery limits for MS should be 75 to 125 percent. Alternately, statistical evaluation of laboratory performance over time for samples of similar matrix and concentration level may be used. In those cases where recovery criteria are not met, the source of error shall be investigated. If a laboratory error is identified and where sufficient sample material remains, all samples in the preparation batch shall be re-prepared and analyzed, unless client-specific DQRs dictate otherwise. The client shall be notified prior to re-preparation if additional costs will be incurred. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or new work scope agreed on.

A MS shall be prepared with each batch of 20 samples and the results reported to the client along with the calculated recovery (see Section 7.2). No adjustment of the client sample results is made in the laboratory report.

NOTE: *Situations may exist where there is no spike material available (e.g., ^{93}Zr). In such cases, method performance must rely on tracers and/or carriers.*

6.2.5 Laboratory Sample Duplicate or Matrix Spike Duplicate

Laboratory duplicates are two aliquots of the same sample (intralaboratory splits) that are taken through the entire sample preparation and analytical process. Spike duplicates are two spiked aliquots of the same sample that are taken through the entire sample preparation and analytical process. Duplicates are used to assess the precision of the preparation and counting process in a client-specific matrix. The degree of agreement between duplicates indicates the reproducibility (precision) of the combined preparation/separation and measurement process.

Disagreement can occur due to analyte concentration differences within the sample matrix (non-homogeneity) that are not amenable to analyst control during the analytical process (e.g., isolated

particles of plutonium in a soil matrix that cannot be reliably sampled using standard laboratory sub-sampling techniques). Disagreement may arise if the method has poor applicability to the analyte/matrix system.

Typically, radiochemical preparations include a sample and sample duplicate. In cases where the sample is not expected to contain concentrations of target analytes sufficient to produce relatively small counting errors, the use of a MS and MSD should be considered.

Radiochemical duplicate relative percent difference (RPD) criterion is set at 20 percent for aqueous liquids and 30 percent for all others. This criterion shall apply when both sample results are >5 times the MDC and the individual uncertainties are < 20 percent. Or alternatively, the duplicates should agree within two standard deviations. The laboratory can also perform an evaluation using the mean difference. The mean difference calculation takes the uncertainty of each individual measurement into account when comparing the two results. The formula for calculating the mean difference is presented in Section 7.4.3.

In those cases where the criteria above are not met, the source of error shall be investigated. If a laboratory error is identified, and where sufficient sample material remains, all samples in the preparation batch shall be re-prepared and analyzed, unless client-specific DQRs dictate otherwise. The client shall be notified prior to re-preparation if additional costs will be incurred. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or new work scope agreed upon.

6.2.6 Tracer

A tracer is a radioactive isotope that chemically mimics and does not chemically interfere with the target radioisotope through radiochemical preparation and separation. For most radiochemical applications, a tracer is considered to be massless. Tracers are added to all samples in an analytical batch (including batch QC samples) such that each sample has a specific measurable activity of the tracer. From the time of spiking, tracers undergo the same chemical processing as the samples. Tracers are counted but may have different emissions (e.g., gamma emitting Sr-85 used for Sr-90 determinations). Any activity effects of a tracer on the final sample counting configuration must be taken into account. The tracer yield is used in the data calculations to correct for any and all sources of analytical losses.

Radiochemical techniques typically employ a tracer, carrier, or MS, or a combination of a MS with a tracer or carrier. A tracer is used to correct radiochemical yield in a specific sample. The amount of tracer recovered through a method reflects the effectiveness of the radiochemical separation for the target analyte. Because a tracer is both radioactive and massless, it can be added to all samples in an analytical batch as a sample-by-sample QC measure (yield). The recovery of the tracer is used to correct for all losses of the target analyte. Sufficient tracer must be used to maintain counting statistics to support client DQO needs.

The tracer may be added to an aliquot of prepared (e.g., leached) or diluted sample prior to specific radiochemical manipulations (e.g., separations). The tracer added at this point can indicate matrix-related effects remaining after preparation but gives no measure of the efficiency

of the original preparation step. Isotopic exchange with the analyte is assumed. The decision on when to spike a sample with tracer is based on the expected analyte activity in the sample, but should be added as early in the analytical process as is practicable.

The isotope activity(ies) in the tracer shall provide sufficient counts such that random counting statistics and background contributions are not significant. However, the source shall not be so radioactive as to cause (1) pulse pileups, (2) dead time that is significantly different from that to be expected from routine samples, or (3) gain shift in the case of pulse height analyzer systems.

The criteria for selection and recovery (maximum and minimum limits) of tracers shall be specified. Tracer materials shall be selected to minimize, and evaluated to establish, contributions to the region(s) of interest for the specific analytes determined. Nominal recovery limits for tracers should be 30 to 110 percent. In those cases where recovery criteria are not met, the source of error shall be investigated. If a laboratory error is identified and where sufficient sample material remains, all affected samples shall be re-prepared and analyzed, unless client-specific DQRs dictate otherwise. The client shall be notified prior to re-preparation if additional costs will be incurred. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or new work scope agreed upon.

NOTE: *High yields with radiochemical tracers are not always of great importance, provided that the yields can be evaluated (e.g., it is common to sacrifice yield to achieve a better separation). Before applying a yield correction, evaluation of whether or not sufficient counting statistics were achieved to make yield correction meaningful shall be made.*

6.2.7 Carrier

For this discussion, a carrier is used to correct radiochemical yield in a specific sample. As with a tracer, carrier recovery is a measure of the amount of analyte lost in performing the procedure. The amount of carrier added shall be sufficient to provide analytical results in the nominal reporting range of the instruments used. The influence of a carrier on counting of the target analyte (e.g., mass attenuation of beta counting) must be addressed during procedure qualification. This affect may be considered as negligible in cases such as in gamma counting.

The carrier may be added to an aliquot of prepared (e.g., leached) sample prior to specific radiochemical manipulations (e.g., separations). The carrier added at this point can indicate matrix-related effects remaining after preparation but gives no measure of the efficiency of the original preparation step. The decision on when to spike a sample with carrier is based on the expected analyte activity in the sample, but should be added as early in the analytical process as is practicable.

The criteria for selection and recovery (maximum and minimum limits) of carriers shall be specified, as use may be considered unique to the specific isotope being determined. Nominal recovery limits for carriers should be 40 to 110 percent. In those cases where recovery criteria are not met, the source of error shall be investigated. If a laboratory error is identified, and where sufficient sample material remains, all affected samples shall be re-prepared and analyzed, unless client-specific DQRs dictate otherwise. The client shall be notified prior to re-preparation

if additional costs will be incurred. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or new work scope agreed upon.

NOTE: *High yields in radiochemistry are not always of great importance, provided the yields can be evaluated (i.e., it is common to sacrifice yield to achieve a better separation). Before applying a yield correction, evaluations of whether or not sufficient measurable mass was achieved to make yield correction meaningful shall be made.*

6.3 RADIOANALYTICAL TECHNIQUES

Analytical techniques are those operations that permit the measurement of a parameter of interest. For the purposes of this document, radiochemical analysis is the measurement of some property (e.g., alpha, beta, or photon emissions) for which there is an instrument response that can be related to the concentration or amount of the radionuclide of interest in a sample or in some material prepared from the sample. The selection of analytical techniques should be based on client DQRs. The QC requirements presented in the subsections that follow are designed to give the analyst information regarding the precision, accuracy, and sensitivity of the analytical process.

6.3.1 Counting Sequence

An analytical sequence or run is defined as those samples counted on any specific detector in a period of time between counter control counts. Thus, by definition, the analytical run starts after the counter control source is counted and ends when the following counter control source is counted.

As a matter of good technique, the sequence of samples counted on a detector, where the detector face is directly exposed to the sample, should be traceable. Gas-flow proportional counters (alpha/beta counting) and silicon-barrier counters (alpha spectrometry) are examples of detector systems where the detector is exposed to the sample and contamination may occur. The sequence reconstruction will allow the analyst to better evaluate problems associated with data that may have been generated on a counter that was contaminated during the course of an analytical sequence.

6.3.2 Verification of Calibration

The calibration verification confirms the acceptability of the calibration. The calibration verification demonstrates that both the standards used and the calibration are accurate. Calibration verification shall be performed before commencement of sample analysis.

The isotope activity in the calibration verification standard shall provide sufficient counts such that random counting statistics and background contributions are not significant. This can be managed by adjusting the isotope activity and the counting time of the standard. However, the source shall not be so radioactive as to cause (1) pulse pileups, (2) dead time that is significantly different from that to be expected from routine samples, or (3) gain shift in the case of pulse height analyzer systems.

Calibration of counting instrumentation used in support of radiochemical measurements often applies over extended periods of time (e.g., years). Only one calibration verification needs to be performed after instrument calibration per geometry. Instrument stability, and thus calibration stability, is monitored by counter control measurements (see Section 6.3.3).

The concept of calibration verification is accomplished in radiochemistry by using one of two methods: independent standards or use of independent measurements. Examples of these concepts are provided below.

6.3.2.1 Use of Independent Standard

An independent standard (see Section 4.4) is prepared in the same geometry as the calibration standard. Standards prepared from a separate lot from the calibration standard are acceptable. The measured activity from the calibration verification standard shall fall within acceptable tolerance limits (as defined in the governing standard operating procedure).

6.3.2.2 Use of Independent Measurement

The calibration standard is measured on an independently calibrated detector for confirmation of the isotope activity(ies). This will confirm the standard was prepared correctly and will provide an accurate basis for the calibration.

6.3.3 Counter Control Source

In radiochemistry, a counter control source (CCS) is used to monitor instrument stability over time. Acceptable performance demonstrates the measurement system is still in control, thus providing assurance the calibration is still valid. A CCS may be prepared from any reliable source, and need not be from nationally or internationally traceable material. Acceptable performance is demonstrated when the concentrations/activities measured fall within established control limits. See Table 4-1 through Table 4-4 for measurement frequency and criteria.

Each analytical (counting) sequence shall be followed by an acceptable counter control measurement prior to the next analytical sequence. Failure justifies corrective action and applies to all samples run since the last acceptable check. If no additional standard or spike information is present at the end of the preceding run, all data generated since the last acceptable counter control check or QC sample shall be considered suspect and investigated.

The CCS should provide adequate counting statistics over the time period for which the source is to be counted. The isotope activity of the CCS shall provide sufficient counts such that random counting statistics and background contributions are not significant. This can be managed by adjusting the isotope activity and the counting time of the source. However, the source shall not be so radioactive as to cause (1) pulse pileups, (2) dead time that is significantly different from that to be expected from routine samples, or (3) gain shift in the case of pulse height analyzer systems.

6.3.4 Backgrounds

Radiochemical measurements typically include a background count. Background counts are a measure of system and/or environmental contributions and a fundamental aspect of the MDC determination. Background count collection frequencies are listed in Table 4-1 through Table 4-4. Background counts are normally subtracted from all subsequent sample counts and shall be recorded.

For counting methodologies where the sample material, or a preparation of it, is introduced directly into the counting chamber (alpha spectrometer or gas proportional counting) the laboratory will take action to verify residual activity from high activity samples does not remain following analysis. The verification shall ensure that instrument background remains within established control limits.

6.4 INORGANIC PREPARATIVE TECHNIQUES

Preparative techniques are those operations used to prepare a sample for analysis. Examples include: digestion, dissolution, extraction, phase partitioning, and/or leaching of a sample material. Separation and/or isolation techniques are also considered preparative if performed before analysis, to facilitate reliable analyte measurement. Simple dilution is not considered a sample preparation technique. Selection of preparative techniques should be based on client DQRs. See the discussion in the subsections that follow and Table 6-2 for frequency requirements used during preparation.

The HASQARD considers the use of either Contract Laboratory Program protocols or associated EPA SW-846 protocols to be acceptable.

Table 6-2. Preparative Requirements for Inorganic Quality Control. (2 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
All Inorganic Techniques Except pH and Biochemical Oxygen Demand			
Preparation blank or method blank ^a	One per batch	< EQL, ≤ 50% regulatory decision level, or ≤ 10% of lowest measured concentration in the samples For Cyanide, Hexavalent Chromium, and Ion Chromatography: <EQL, or 10% of the regulatory limit, or 10% of the lowest sample concentration, whichever is greater	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.

Table 6-2. Preparative Requirements for Inorganic Quality Control. (2 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
BS -or- LCS	One per batch	80 to 120% or statistical ^b Vendor or statistical ^b	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Duplicate or MSD	One per batch	≤ 20% RPD when result > EQL for liquids ≤ 35% RPD when result is > EQL for solid samples	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
MS	One per batch	Recommended 75 to 125% or statistical	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
pH			
Duplicate	Every 10 samples	N/A	Discuss in narrative.
Biochemical Oxygen Demand			
Dilution water blank	One per batch	Dissolved Oxygen <0.2 mg/L	Investigate. Discard all data for tests using this water or clearly identify such samples in data records.
Seed Control	One per batch	Slope method: Dissolved Oxygen-axis intercept should be < 0.2 mg/L Ratio method: Depletions/mL within ±30%	Investigate. Change seed source.

^a Shall be applied to original preparation stage.

^b Laboratory-developed procedures shall either meet specifications or show statistical basis for alternative criteria. Alternative criteria are acceptable if they meet client DQRs.

6.4.1 Preparation Batch

A preparation batch is a group of samples, of similar matrix type, prepared at the same time. A batch shall not exceed 20 client samples. More than 20 samples can be prepared at the same time if the required numbers of QC samples are performed for each batch. If clients do not specify project-specific QC, the laboratory may combine up to 20 samples of similar matrix type for preparation with only one duplicate (or MSD) and MS required. In the case of process testing or unique client requirements, QC elements such as a sample duplicate (or MSD) and MS

may be performed for every 20 client-specific samples received. However, the preparation blank and LCS/BS requirement would apply to each batch of samples.

A sample or series of samples that do not require preparation or separation prior to analysis would not fall under the requirements in this section. Additionally, limited sample quantity may limit the laboratory's ability to meet the duplicate and MS requirements. In such cases, alternative approaches should be considered to demonstrate sample precision and accuracy. Unique client requirements shall be documented and agreed on by the laboratory and the client before work begins.

6.4.2 Preparation Blank (Method Blank)

The sample preparation blank (method blank) is used to monitor contamination resulting from the sample preparation process. The preparation blank is generally distilled or deionized water, which is subjected to the same processing as the samples, including all reagent additions. The laboratory is also free to use a matrix more closely related to the actual samples processed, provided the matrix is free of contamination from analytes of interest (e.g., clean soil or sand for solid matrices). Interferences and/or unique ancillary contaminants produced by the blank matrix would be expected to be similar to that of the sample.

The preparation blank volume or weight shall be approximately equal to the sample weight or volume being processed and shall be presented in the same context as the samples. Preparation or method blanks shall be prepared with each batch of samples processed at the same time.

Preparation or method blank acceptability shall be demonstrated as follows: (1) the blank shall be less than the EQL of the associated samples, or (2) if the blank is equal to or above the EQL, it shall not exceed 10 percent of the measured concentration present in the associated samples, or (3) when a decision level is specified, the blank shall not exceed 10 percent (for cyanide, hexavalent chromium, and IC) or 50 percent (for others) of the decision level unless (2) above applies.

NOTE: *The laboratory must be capable of achieving an EQL less than or equal to 10 percent (for cyanide, hexavalent chromium, and IC) or 50 percent of the decision level or must negotiate an acceptable alternative. All affected samples in the preparation batch will be re-prepared and analyzed if the preparation blank (method blank) fails to meet the acceptance criteria.*

All affected samples in the preparation batch will be re-prepared and analyzed if the preparation blank fails to meet one of the acceptance criteria unless client-specific DQRs dictate otherwise. The client shall be notified prior to such actions when additional costs will be incurred.

The results of the preparation blank analysis and impacts on data shall be reported to the client as part of routine reports. Preparation blank results are not subtracted from sample results unless client DQRs specify otherwise, in which case, the case narrative accompanying the results should state that blank subtraction was used.

6.4.3 Laboratory Control Sample or Blank Spike

An LCS or BS is used to monitor the effectiveness of the sample preparation process. The LCS is a material similar in nature to the sample being processed containing the analyte(s) of interest (e.g., standard reference material). An LCS, if available, shall be prepared with each batch of samples processed at the same time. The BS is distilled or deionized water, or other suitable substrate, spiked with the analytes(s) of interest. A BS is normally used when an appropriate LCS is unavailable.

BS control is demonstrated by target analytes being within either the preset limit of 80 to 120 percent or within statistically determined limits when the ± 20 percent criteria cannot be reliably achieved.

LCS acceptability is demonstrated by target analytes being within established control or acceptance limits. Control limits are either provided by the vendor or statistically determined by multiple analyses over time. For the LCS, the vendor-supplied precision may affect the acceptance limits applied to the analyte.

The laboratory must ensure that each method used for a given scope of work is capable of meeting client precision and accuracy requirements or the laboratory must negotiate alternative requirements.

All samples in the preparation batch shall be re-prepared and analyzed for those analytes in which the acceptance criteria for the LCS or BS have not been met. In limited cases, results may be acceptable for reporting provided the laboratory can demonstrate that the client DQR was still achieved. The client shall be notified prior to re-preparation if additional costs will be incurred.

The LCS/BS results should be reported to the client. No adjustment of client sample results based on LCS recovery is made in the laboratory report.

6.4.4 Matrix Spike

A MS is a client sample that has been spiked with the analyte(s) of interest and processed in the same manner as the sample. The MS is used to monitor method performance in a specific sample matrix. MS results are a measure of the accuracy in the measurement of the analyte(s) of interest present in the client sample matrix.

When the sample concentration is unknown, spiking is typically performed at a level that is one of the following: (1) equivalent to the regulatory threshold, (2) specified by method, or (3) one to five times the EQL. Otherwise, the spiking should be performed at a level equivalent to one to two times that of the sample. When the concentration of the analyte in the original sample is greater than 0.1 percent, no MS is required unless specified by client.

For inorganic analysis, MS control is demonstrated when target analytes are within established control limits. Control limits are established by one of the following: (1) regulatory requirement, (2) the client via DQRs for a particular project or program, or (3) laboratory

performance over time. The recommended criterion for most inorganic analysis is recovery within 75 to 125 percent.

If the MS recovery fails to meet the criteria, the batch results shall be investigated for sources of error. Re-preparation and/or re-analysis should be conducted as necessary based on the DQO/DQR. The goal is to ensure that limitations on the data caused by the sample matrix and represented by MS performance are adequately portrayed and discussed in the report to the client.

In those instances where the sample concentration significantly exceeds the amount of spike added in the prepared samples, the data must be further evaluated to determine if the recovery of the spiked sample is meaningful.

A MS shall be prepared with each batch of 20 samples and the results reported to the client along with the calculated recovery. No adjustment of the client sample results is made in the laboratory report. MS performance shall be discussed in the report narrative.

In the case where a sample matrix cannot be spiked at the time of original preparation, a post-digestion spike (PDS) shall be performed (Section 6.5.8). The term "matrix spike" can only be used when the sample is spiked at original preparation.

6.4.5 Laboratory Sample Duplicate or Matrix Spike Duplicate

Laboratory sample duplicates are two aliquots of the same sample (intralaboratory split) that are taken through the entire sample preparation and analytical process. Laboratory duplicates are used to assess the precision of the preparation and analysis process in a client-specific matrix.

MSDs are two spiked aliquots of the same sample that are taken through the entire sample preparation and analytical process. In cases where the sample is not expected to contain reasonable concentrations (e.g., analyte concentrations greater than EQL) of the analytes of interest, duplicate sample results will not provide a reliable estimate of precision. In these cases, MSDs are used to demonstrate analytical precision in the client sample.

The degree of agreement between duplicates indicates reproducibility of the combined preparation/separation and measurement process (precision).

Disagreement can occur due to analyte concentration differences within the sample matrix (non-homogeneity) that are not amenable to analyst control during the analytical process (e.g., isolated particles of lead in a soil matrix that cannot be reliably sampled using standard laboratory subsampling techniques). Disagreement may arise if the method has poor applicability to the analyte/matrix system.

One set of laboratory duplicates (or MS/MSD) is required for each batch of samples. Precision is estimated by calculating the RPD of the duplicate analysis (see Section 7.1.2). Upon receipt of instructions from the client, additional replicates can be performed. These additional samples will increase the likelihood of detecting non-uniformly distributed analytes in the client sample.

It will also allow for a more accurate estimate of the variability of the overall analytical performance on client-specific samples/matrices. When more than two replicates are used, precision is expressed in terms of relative standard deviation (RSD) (Section 7.1.1).

Typically, inorganic analyses include a sample and a sample duplicate because a high probability exists that the majority of those analyte(s) of interest will be detected in the sample. The inorganic duplicate RPD criterion is normally set at 20 percent for liquids and 35 percent for solids when the concentration is >QL.

In those cases where the criteria above are not met, evaluation of the source of error and impact on client DQRs shall be performed. When client DQRs cannot be met, the client shall be notified; results shall either be accepted by the client or a new work scope (methodology) agreed upon.

Duplicate (or MSD) results shall be reported to the client along with the calculated RPD. Duplicate results shall be discussed in the report narrative.

6.5 INORGANIC ANALYTICAL TECHNIQUES

Analytical techniques are those operations that permit the measurement of a parameter of interest. Analysis is the measurement of some property for which there is an instrument response that can be related to the concentration or amount of the substance of interest in a sample or in some material prepared from the sample. Selection of the analytical technique should be based on client DQRs.

HASQARD considers the use of either Contract Laboratory Program protocols or associated EPA SW-846 protocols to be acceptable.

The QC requirements presented in the subsections that follow are designed to verify and document proper instrument operation and to give the analyst information regarding the precision, accuracy, and sensitivity of the analytical process.

6.5.1 Analytical Run or Sequence

An analytical run or sequence is defined as a group of samples analyzed together that may include one or more preparation batches. Each analytical sequence has a prescribed number and type of QC standards associated with it, which are analyzed in a prescribed order. The analytical sequence is an important aspect of the analytical work performed because it allows the analyst and subsequent data reviewers to determine if there are trends in sample results or QC that are related to the order in which samples were analyzed. This may allow the elimination of unnecessary re-analysis due to a QC failure (e.g., cross-contamination between samples) during an analytical sequence. Therefore, the order in which samples are analyzed will be traceable to the analytical sequence.

The analytical sequence typically starts with either calibration or confirmation that the calibration is still valid. Table 6-3 lists the QC sample frequency requirements used during inorganic analysis.

For most inorganic analyses, the analytical sequence ends with a continuing calibration standard and blank. More than one batch of samples can be analyzed in an analytical sequence as long as continuing calibration control is maintained.

Table 6-3. Analytical Requirements for Inorganic Quality Control. (5 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
Inductively Coupled Plasma Spectrometry and Flame Atomic Absorption			
ICV	Immediately after calibration (typically mid-point region)	90 to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
CCV	Every 10 samples and at the end of the run	90 to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest and re-analyze affected samples
Initial calibration blank (ICB)	After ICV	< EQL	Investigate failure for analytes of interest. Evaluate and/or correct. Recalibrate for failed analytes of interest when applicable.
Continuing calibration blank (CCB)	After each CCV	< EQL	Investigate failure for analytes of interest. Evaluate and/or correct. Recalibrate for failed analytes of interest when applicable and re-analyze affected samples.
Low-level standard ^a	At the beginning of an analysis (but not before ICV and ICB)	Recommended 70 to 130%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Interference check standard ^b	After ICV and ICB and at the end of the run	80 to 120%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.

Table 6-3. Analytical Requirements for Inorganic Quality Control. (5 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
Serial dilution	One per analytical batch	≤ 10% difference when analyte >10 times EQL after 5-fold dilution	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
PDS	When MS fails or when a new or unusual matrix is encountered	Recommended 80 to 120%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Inductively Coupled Plasma/Mass Spectrometry			
ICV	Immediately after calibration (typically mid-point region)	90 to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
CCV	Every 10 samples and at the end of the run	90 to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest and re-analyze affected samples.
ICB	After ICV	< EQL	Investigate failure for analytes of interest. Evaluate and/or correct. Recalibrate for failed analytes of interest when applicable.
CCB	After each CCV	< EQL	Investigate failure for analytes of interest. Evaluate and/or correct. Recalibrate for failed analytes of interest when applicable and re-analyze affected samples.
Interference check standard	After ICV and ICB and every 12 hours	Monitor for interferences	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative and flag data accordingly.
Serial dilution	Contingent QC performed in accordance with the analytical method used (see Section 6.5.9)	≤ 10% difference when analyte > 100 times IDL	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.

Table 6-3. Analytical Requirements for Inorganic Quality Control. (5 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
PDS	When MS or serial dilution fails or when new or unusual matrix is encountered	75 to 125%	Evaluate. If laboratory error, re-prepare and analyze. Perform dilution test or method of standard additions. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Internal standard	Every sample, QC sample ^c	>30 to ≤120%	Perform serial dilution. Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Mercury (e.g., Cold Vapor Atomic Absorption – Manual and Automated)			
ICV	Immediately after calibration	80 to 120%	Investigate failure. Correct. Recalibrate when applicable.
ICB	After ICV	< EQL	Investigate. Evaluate and/or correct.
CCV	Every 10 samples and at the end of the run.	80 to 120%	Evaluate. Reanalyze. Recalibrate when applicable. Reanalyze affected samples.
CCB	After each CCV	< EQL	Investigate. Evaluate and/or correct. Reanalyze affected samples.
Low-level standard	After ICV and ICB	Recommended 70 to 130%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Serial dilution	If MS/MSD fails	≤ 10% difference when analyte >10 times IDL after 5-fold dilution	Evaluate. If laboratory error, re-prepare and analyze. Perform method of standard additions and/or evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Cyanide (All Techniques, Except Titrimetric Methods)			
ICV	Immediately after calibration	85 to 115%	Investigate. Correct. Reprepare and .reanalyze.
ICB	After ICV	< EQL	Investigate. Evaluate and/or correct.

Table 6-3. Analytical Requirements for Inorganic Quality Control. (5 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
CCV	Every 10 samples and at the end of the run	85 to 115%	Evaluate. Recalibrate when applicable and re-analyze affected samples
CCB	After CCV	< EQL	Reanalyze. Investigate. Evaluate and/or correct. Reanalyze affected samples
Low-level standard	After ICV and ICB	Recommended, 70 to 130%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Graphite Furnace Atomic Absorption			
ICV	Immediately after calibration	90 to 110%	Investigate. Correct. Recalibrate.
CCV	Every 10 samples and at the end of the run	80 to 120%	Investigate. Correct. Recalibrate and/or re-analyze affected samples.
ICB	After ICV	< EQL	Investigate. Evaluate and/or correct.
CCB	After each CCV	< EQL	Investigate failures. Correct. Recalibrate and/or re-analyze affected samples.
Low-level standard	After ICV and ICB	Recommended 75 to 125%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
PDS	When MS fails	Recommended 75 to 125%	Evaluate. If laboratory error, re-prepare and analyze. Evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Ion chromatography			
ICV	After initial calibration	90 to 110%	Investigate. Correct. Reanalyze.
ICB	After ICV	< EQL or 5% of the lowest sample result with client consent.	Investigate. Correct. Reanalyze.

Table 6-3. Analytical Requirements for Inorganic Quality Control. (5 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
CCV	Beginning of analytical sequence if initial calibration is not run, every 10 samples, and at the end of the run	90 to 110%	Investigate. Correct. Recalibrate when applicable and reanalyze affected samples.
CCB	After CCV	< EQL or 5% of the lowest sample result with client consent.	Reanalyze. Investigate. Correct. Recalibrate when applicable and re-analyze affected samples.
Low-level standard	After ICV and ICB	Recommended 50 to 150%	Investigate for error. Discuss in narrative.
pH			
CCV	After every 10 samples and at the end of the run	≤ 0.1 pH unit	Rerun all samples since last valid CCV.
Ion Selective Electrode and Colorimetric Methods (e.g., Ammonia, Hexavalent Chromium, Fluoride)			
ICV	Immediately after calibration for working curve technique, prior to analysis of samples for all other techniques.	Based on long-term statistical performance or 90 to 110% as applicable.	Recalibrate.
ICB	After ICV	< EQL	Recalibrate.
CCV	After every 10 samples and at the end of the run (not applicable to titration methods).	Based on long-term statistical performance or 90 to 110% as applicable.	Investigate. Correct. Recalibrate when applicable and re-analyze affected samples
CCB	After each CCV	< EQL	Investigate. Correct. Rerun affected samples since last valid CCB.
Titrimetric Methods			
ICB	1 per batch	< EQL	Investigate. Correct. Reanalyze.
Titrant Verification	1 per batch	80 to 120%	Investigate failures. Correct. Re-standardize titrant and re-analyze samples.

^aThis standard equals the estimated quantitation limit standard for flame atomic absorption.

^bNot required for flame atomic absorption.

^cCalibration verification standards and blanks may have more stringent internal standard requirements based on the analytical method.

6.5.2 Initial Calibration Verification

The ICV analytical standard is used to confirm the accuracy of the calibration and the standards used for calibration. Acceptable performance of the ICV demonstrates that both the standards used and the instrument are functioning properly. The ICV is prepared from a source other than that used to prepare the calibration standards (see Section 4.0).

Most inorganic techniques are subject to routine, frequent recalibration. The ICV is required whenever the system is recalibrated. The ICV shall be run following calibration and before analysis of client samples.

Acceptance criteria for major inorganic instrument systems or analyses can be found in Table 6-3. Failure of the ICV indicates instrument and/or standard problems that must be evaluated and corrected before any client samples are processed for the analytes of interest.

6.5.3 Continuing Calibration Verification

The CCV analytical standard is used to monitor instrument stability over time. Acceptable performance demonstrates continued appropriateness of the calibration, indicating that the system is still in control. The CCV may be prepared from any reliable source and need not be nationally or internationally traceable. The ICV standard may also be used as the CCV.

Each inorganic analytical system shall include periodic checks on the stability of the instrument calibration. The CCV acceptance criteria and frequency is discussed in Table 6-3. Failure indicates that the analytical system has drifted out of control and requires corrective action for the analytes of interest. Samples analyzed after the last acceptable CCV shall be re-analyzed. Reanalysis applies to specific analyte failure. In limited cases, isolated analyte failures may be tolerated if sample results still meet the client DQRs. Reporting results in such cases requires justification in the report to the client.

6.5.4 Initial and Continuing Calibration Blanks

Initial calibration blanks (ICBs) and continuing calibration blanks (CCBs) monitor effects such as contamination and instrument response drift during routine analysis. The ICB/CCB is a reagent blank, prepared similarly to the standards but not subjected to preliminary sample preparation except for techniques in which the preparation is an integral part of the analysis. In these cases, the preparation blank or method blank can be considered the equivalent of the ICB or CCB. The generally accepted criterion for these blanks is that they are below the EQL for each analyte of interest. When an analyte exceeds this criterion, the analysis shall be investigated for potential impact. Samples with concentrations or activities exceeding the blank contamination level by a factor of 20 or more can be reported unless client requirements dictate otherwise. In all other cases, all samples analyzed since the last acceptable ICB or CCB shall be analyzed for the specific analyte failure.

For inorganic compounds, each ICV shall be followed by an ICB and each subsequent CCV shall be followed by a CCB. This protocol indicates potential carry-over effects (e.g., carryover of

residual material from one sample to the next in the sequence), which should be avoided by appropriate method design (e.g., adequate rinse time between samples).

6.5.5 Internal Standards

An internal standard is an analyte that is similar to the analyte(s) of interest in terms of its analytical response, but which is not normally expected to be found in the sample. Internal standards are added to every standard, blank, MS, MSD, and sample before analysis. Internal standards are used as the basis for quantitation of the target analytes of interest.

Internal standards are routinely used in ICP/MS analysis although they may be appropriate to other types of analysis. Selecting appropriate internal standards shall be method- and analyte-list specific because all results are normalized based on internal standard performance. Laboratory procedures shall specify internal standards used and associated acceptance criteria.

6.5.6 Low-Level Standard

The low-level standard is used to monitor instrument performance in the region at or near the EQL and is routinely applied to inorganic systems to monitor sensitivity in the EQL region.

For ICP spectrometry systems, the low-level standard should be prepared at approximately two times the EQL. The majority of other inorganic techniques employ a low-level standard that is at or near the EQL (see Table 6-3). In those cases where it is used as part of instrument calibration, a separate low-level standard is not required.

A recovery between 70 and 130 percent is recommended. If the low-level standards fail to meet this criterion, all client samples whose results are less than 10 times the EQL should be evaluated for impact, and any limitations noted in the report narrative.

6.5.7 Interference Check Standards

Interference check standards are typically applied in ICP systems (e.g., ICP and ICP/MS). The interference check normally consists of two standards. The first standard contains known concentrations of the major interfering elements that will provide an adequate test of interelement correction factors. The second standard contains both the major interferents and the majority of other analytes tested. The major interferents are spiked into the standards at significant concentrations that are expected to produce an interference effect. All other analytes are spiked at relatively low levels. Data from both standards, when corrected, should recover between 80 and 120 percent for all analytes tested, or an interelement correction is considered inadequate. The first standard, containing only the major interferents of concern, should produce no analyte concentration with an absolute value in excess of the EQL. Instruments capable of showing negative results do not require the second standard that contains both interferents and additional analytes tested.

6.5.8 Post-Digestion Spike

For inorganic analytes of interest, a PDS is a spike added to the sample after preliminary preparation, usually just before analysis. The PDS is used to indicate matrix-related interferences on the analytical system that may still be present in the sample following digestion. The PDS is normally used when a MS failure occurs. This technique is typically used for ICP analysis, but is also appropriate to other analyses.

PDS performance can be used to identify problems caused by sample matrix effects during preparation and/or measurement. In the case of unusual matrix effects only during the preparation step, the MS will fail but the PDS will pass. If both the MS and PDS fail, the failure is due to matrix effects in both the preparation and measurement steps.

Acceptable recovery is generally 75 to 125 percent for the PDS (see Section 7.2). If the PDS meets the acceptance criteria indicating that MS failure occurred during the sample preparation step, all client samples in the batch should be flagged in the laboratory report and the sample preparation problem pointed out in the case narrative. If the PDS fails to meet the acceptance criteria, this indicates a failure in both the sample preparation and measurement steps caused by matrix problems. All results of client samples in the batch should be flagged and the reasons discussed in the case narrative.

Re-analysis of the samples using different preparation and/or measurement procedures should be considered by the laboratory if alternative procedures are available, which in the judgment of qualified chemists, offer a reasonable solution to the problem(s). Prior to re-analysis, client concurrence must be obtained because the procedural changes may violate mandated existing regulatory or project requirements.

6.5.9 Serial Dilution

Serial dilution is used when new or unusual matrices are encountered as an indicator of potential matrix-related interferences associated with analysis. It is simply a five-fold dilution of a sample (after all preparation steps are complete) followed by analysis. Serial dilution is only performed when a sufficient number of target analyte concentrations exceed 10 times the EQL in the client sample.

The serial dilution is designed to indicate potential problems (e.g., high solids effects) that can impact sample uptake, resulting in analyte measurement differences. In these cases, results would begin to vary beyond the 10 percent criteria because of sample aspiration and the subsequent effect on analyte species detected. The serial dilution does not replace a sample dilution necessary to maintain a sample in optimum instrument performance range.

A percent difference between the original and diluted sample results of 10 percent or less indicates no significant matrix effects during the measurement process. The client sample results in the batch that doesn't meet the serial dilution acceptance criteria should be noted, and the possible matrix effects discussed in the case narrative.

6.5.10 Method of Standard Additions

The method of standard additions consists of a blank and at least three standards, to which aliquots of the sample are added. The standards used should be approximately 50 percent, 100 percent, and 150 percent of the expected sample concentration. The method of standard additions can be used in lieu of instrument calibration because each sample essentially has its own calibration. However, the QC presented in Section 6.4 is still required (including “auto-zeroing” on the calibration blank). The method of standard additions is meant to compensate for a sample matrix effect that enhances or depresses analyte signals.

6.6 ORGANIC PREPARATIVE TECHNIQUES

Preparative techniques are those operations used to prepare a sample for analysis. Examples of preparative techniques include digestion, dissolution, extraction, phase partitioning, and/or leaching of a sample material. Separation and/or isolation techniques are also considered preparative if performed before analysis, to facilitate reliable analyte measurement. Simple dilution is not considered a sample preparation technique. Selection of preparative techniques should be based on client DQRs.

HASQARD considers the use of either Contract Laboratory Program protocols or associated EPA SW-846 protocols to be acceptable.

Table 6-4 lists the required frequency of QC samples to be included during sample preparation.

Table 6-4. Preparative Requirements for Volatile, Semi-Volatile, and Gas Chromatography Quality Control. (2 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
Method blank	One per batch	≤ EQL (see Section 6.6.2)	Investigate against samples and client DQRs. Correct. Re-prepare and analyze affected samples
BS -or- LCS	One per batch	Vendor/method/ statistical (see Section 6.6.3)	Investigate, evaluate against DQRs, correct and re-prepare/analyze as applicable.
	One per batch	Vendor/statistical (see Section 6.6.3)	
MS and MSD (precision)	One set per batch	See Section 6.6.5	Evaluate. If laboratory error, re-prepare and analyze. If matrix-driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.

Table 6-4. Preparative Requirements for Volatile, Semi-Volatile, and Gas Chromatography Quality Control. (2 sheets)

Quality Control Requirements	Frequency	Criteria	Corrective Action
MS and MSD (accuracy)	One set per batch	See Section 6.6.4	Evaluate. If laboratory error, re-prepare and analyze. If matrix-driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Surrogate	Each sample, QC sample, and standard	See Section 6.6.6	Evaluate. If laboratory error, re-prepare and analyze. If matrix-driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Total Carbon, Total Inorganic Carbon, and Total Organic Compound			
Duplicate	One per batch	≤ 20% RPD when > 10 times IDL	Evaluate. If laboratory error, re-prepare and analyze. If matrix-driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
MS	One per batch	Recommended 75 to 125%	Evaluate. If laboratory error, re-prepare and analyze. If matrix-driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Blank spike -or- Laboratory control sample	One per batch	80 to 120% or statistical Vendor or statistical	Investigate, evaluate against DQRs, correct, re-prepare, and analyze as applicable.
Method blank	One per batch	< EQL	Investigate, evaluate against DQRs, correct, re-prepare, and analyze as applicable.

6.6.1 Preparation Batch

A preparation batch is a group of samples, of similar matrix type, prepared at the same time. A batch shall not exceed 20 client samples. More than 20 samples can be prepared at the same time if the required numbers of QC samples are analyzed for each batch. If clients do not specify project-specific QC (which requires the laboratory to select client samples for duplicates and MSs), the laboratory may combine up to 20 samples of similar matrix type for preparation with only one MSD (or sample duplicate) and MS required. In the case of process testing or unique client requirements, QC elements such as a sample duplicate (or MSD) and MS may be analyzed for every 20 client-specific samples received. However, the preparation blank and LCS or BS requirements are always applied to each batch of samples.

A sample or series of samples that do not require preparation or separation prior to analysis would not fall under the requirements in this section. Additionally, limited sample quantity may limit the laboratory's ability to meet the duplicate and MS requirements. In such cases, alternative approaches should be considered to demonstrate sample precision and accuracy. Unique client requirements shall be documented and agreed on by the laboratory and the client before work begins.

6.6.2 Preparation Blank (Method Blank)

The sample preparation blank (method blank) is used to monitor contamination resulting from the sample preparation process. The preparation blank is generally distilled or deionized water, which is subjected to the same processing as the samples, including all reagent additions. The laboratory is also free to use a matrix more closely related to the actual samples processed, provided the matrix is free of contamination from analytes of interest (e.g., clean soil or sand for solid matrices). Interferences and ancillary contamination produced by the blank material would be expected to be similar to that of the sample.

The preparation blank volume or weight shall be approximately equal to the sample weight or volume being processed and shall be presented in the same context as the samples. The blank should be evaluated for its contribution to the sample, based on how the sample was prepared. A method blank shall be prepared with each batch of samples processed at the same time.

Preparation or method blank acceptability shall be demonstrated as follows: (1) the blank shall be less than the EQL of the associated samples, or (2) if the blank is equal to or above the EQL, it shall not exceed 5 percent of the measured concentration present in the associated samples, or (3) when a decision level is specified, the blank shall not exceed 5 percent of the decision level unless (2) above applies.

NOTE: *The laboratory must be capable of achieving an EQL less than or equal to 5 percent of the decision level or must negotiate an acceptable alternative.*

As a special requirement, the concentration of the following analytes shall be less than five times the EQL.

- Methylene chloride
- Acetone
- 2-butanone
- Phthalate esters.

All samples in the preparation batch will be re-prepared and analyzed if the preparation blank (method blank) fails to meet one of the acceptance criteria for an analyte of interest unless client DQRs dictate otherwise. The client shall be notified prior to re-preparation if additional costs will be incurred.

The results of the preparation blank analysis should be reported to the client as a part of routine reports. Preparation blank results are not subtracted from sample results unless client DQRs specify otherwise, in which case the narrative accompanying the results should state that blank subtraction was used.

Preparation blanks or method blanks shall be prepared with each batch of samples.

6.6.3 Laboratory Control Sample or Blank Spike

An LCS or BS is used to monitor the effectiveness of the sample preparation process. The LCS is a material similar in nature to the sample being processed that contains the analyte(s) of interest (e.g., standard reference material). The LCS shall contain the number of analytes of interest as specified by the mandated test method or other regulatory requirement or as requested by the client. An LCS, if available, shall be prepared with each batch of samples processed at the same time. The BS is distilled or deionized water, or other suitable substrate, spiked with the analytes(s) of interest. A BS is normally used when an appropriate LCS is unavailable. For organic preparations, the method blank, spiked with surrogates, can be used to meet the BS requirement.

BS control is demonstrated by target analyte recoveries within administrative limits of 70 to 130 percent, or within laboratory statistical control limits (when sufficient data are available to establish such limits.)

LCS acceptability is demonstrated by target analytes being within established control or acceptance limits. Control limits are either provided by the vendor or statistically determined by multiple analyses over time. For the LCS, the vendor-supplied precision may affect the acceptance limits applied to the analyte.

All samples in the preparation batch shall be re-prepared and analyzed for those analytes in which the acceptance criteria for the LCS or BS have not been met. In limited cases, results may be acceptable for reporting provided the laboratory can demonstrate that the client DQR was still achieved. The client shall be notified prior to re-preparation, if additional costs will be incurred.

An LCS or BS shall be prepared with each batch of samples and the results reported to the client. No adjustment of client sample results based on LCS or BS recovery is made in the laboratory report.

6.6.4 Matrix Spike

A MS is a client sample that has been spiked with the analyte(s) of interest and processed in the same manner as the sample. The MS is used to monitor method performance in a specific sample matrix. MS results are a measure of the bias (i.e., difference from true value) in the measurement of the target analytes introduced by the client sample matrix.

When the sample concentration is unknown, spiking is typically performed at a level that is one of the following: (1) equivalent to the regulatory threshold, (2) specified by method, or (3) one to five times the EQL. Otherwise, the spiking should be performed at a level equivalent to one to

two times that of the sample. When the concentration of the analyte in the original sample is greater than 0.1 percent, no MS is required.

The analytes to be spiked shall be as specified by the mandated test method. Any permit specified analytes, as specified by regulation or client requested analytes shall also be included.

For organic analysis, MS control is demonstrated when target analytes are within established control limits. Control limits are established by one of the following: (1) method protocol, (2) regulatory requirement, (3) the client via DQRs for a particular project or program, or (4) laboratory performance over time.

If the MS recovery fails to meet criteria, the batch shall be investigated for sources of error. Re-preparation and/or re-analysis should be conducted as necessary based on the DQO/DQR. The goal is to ensure that limitations on the data caused by the sample matrix, and represented by MS performance, are adequately portrayed and discussed in the report to the client.

In those instances where the sample concentration significantly exceeds the amount of spike added in the prepared samples, the data must be further evaluated to determine if the recovery of the spiked sample is meaningful.

A MS shall be prepared with each batch of 20 or fewer samples, and the results reported to the client along with the calculated recovery (see Section 7.3). No adjustment of the client sample results is made in the laboratory report.

6.6.5 Laboratory Sample Duplicate or Matrix Spike Duplicate

Laboratory sample duplicates are two aliquots of the same sample (intralaboratory split) that are taken through the entire sample preparation and analytical process. Laboratory duplicates are used to assess the precision of the preparation and analysis process in a client-specific matrix. Agreement between duplicates indicates the reproducibility of the combined preparation, separation, and measurement process (precision).

MSDs are two spiked aliquots of the same sample that are taken through the entire sample preparation and analytical process. In cases where the sample is not expected to contain reasonable concentrations of the analytes of interest, duplicate sample results will not provide a reliable estimate of precision. In these cases, MSDs are used to demonstrate analytical precision in the client sample.

Disagreement can occur due to analyte concentration differences within the sample matrix (non-homogeneity) that are not amenable to analyst control during the analytical process. Disagreement may arise if the method has poor applicability to the analyte/matrix tested. Typically, organic analyses include a MS and MSD because a low probability exists that the majority of those analytes of interest will be detected in the sample.

Organic duplicate RPD criteria vary widely according to analyte and method. They are very method/matrix dependent. Acceptance criteria are established by one of three procedures:

- (1) specified by regulatory requirement, (2) specified by the client for a particular project, or
- (3) laboratory performance over time for samples with similar matrices and concentration ranges.

One set of MS/MSDs is required for each batch of samples. Precision is calculated using the RPD (see Section 7.1.2). Additional replicates may be performed if requested by the client. These additional samples will increase the likelihood of detecting non-uniformly distributed analytes in the client sample. It will also allow for a more accurate estimate of the variability of the overall analytical performance on client-specific sample matrices. When more than two replicates are used, precision is expressed in terms of the RSD (see Section 7.1.1).

The results of duplicate (or MSD) analyses are reported to the client along with the calculated RPD for each analyte.

6.6.6 Surrogates

A surrogate is a compound or analyte that is added to all samples (both client samples and QC samples) prior to preparation. The surrogate is typically similar in chemical composition to the compound or analyte being determined, yet not normally encountered in most samples. Surrogates are expected to respond to the preparation and measurement systems in a manner similar to the analytes of interest.

The criteria for selection and recovery of surrogates are generally specific to the method and compounds being detected. Each method that uses surrogates shall specify instructions for surrogate introduction and use. For organic analysis, surrogate control is demonstrated when they are within established control limits. Control limits are established by one of the following: (1) regulatory requirement, (2) the client via DQRs for a particular project or program, or (3) laboratory performance over time.

Surrogate recoveries are reported as measured (i.e., no sample recovery corrections are performed based on surrogate recovery). Because surrogates are added to all standards, samples, and QC, they are a useful tool in evaluating overall method performance in a given matrix. If surrogate recovery fails to meet criteria, the sample results shall be investigated for sources of error. Re-preparation and/or re-analysis should be conducted as necessary based on the DQO/DQR. The goal is to ensure that limitations on the data caused by the sample matrix, and represented by surrogate performance, are adequately portrayed and discussed in the report to the client.

6.7 ORGANIC ANALYTICAL TECHNIQUES

Analytical techniques are considered those operations that permit the measurement of a parameter of interest. Analysis could be considered measurement of some property for which there is an instrument response that can be related to the concentration or amount of the substance of interest in a sample or in some material prepared from the sample. The selection of analytical technique should be based on client DQRs. HASQARD considers the use of either Contract Laboratory Program protocols or associated EPA SW-846 protocols to be acceptable.

The QC requirements presented below are designed to verify and document proper instrument operation and to give the analyst information regarding the precision, accuracy, and sensitivity of the analytical process.

6.7.1 Analytical Sequence (Run)

An analytical run or sequence is defined as a group of samples analyzed together that may include one or more preparation batches. Each analytical sequence has a prescribed number and type of QC standards associated with it, which are analyzed in a prescribed order. The analytical sequence is an important aspect of the analytical work performed because it allows the analyst and subsequent data reviewers to determine if there are trends in sample results or QC that are related to the order in which samples were analyzed. This may allow the elimination of unnecessary re-analysis due to a QC failure (e.g., cross-contamination between samples) during an analytical sequence. Therefore, the order in which samples are analyzed will be traceable to the analytical sequence.

The analytical sequence typically starts with either calibration or calibration verification to confirm the calibration is still valid. Table 6-5 through Table 6-8 list QC sample frequency requirements used during organic analysis. The run ends based on analytical clock expiration for organic analyses by GC/MS. For the GC and carbon analysis, the run ends based on continuing calibration performance.

Confirmation analyses shall be performed on organic tests such as pesticides, herbicides, or acid extractables when recommended or required by the analytical test method, except when the analysis involves the use of a mass spectrometer. When confirmation analyses are required by a test method, they shall be performed unless stipulated in writing by the client. All confirmation analyses shall be documented.

6.7.2 Initial Calibration Verification

The ICV is a standard used to confirm the acceptability of the calibration and the standards used to prepare the calibration. Acceptable performance of the ICV demonstrates that both the standards used and the instrument are functioning properly. The ICV is prepared from a source other than that used to prepare the calibration standards (see Section 4.0).

Analytical measurement systems for which calibration applies over an extended period of time (i.e., months for some GC/MS methods) normally use the ICV only at the time of calibration. Subsequent routine performance checks are made using the equivalent of a CCV (see Section 6.7.3).

Analytical measurement systems that are calibrated frequently and for which calibration standards are routinely prepared normally follow calibration with an ICV.

Acceptance criteria for major instrument systems or analyses can be found in Table 6-5 through Table 6-8. Failure of the ICV indicates instrument and/or standard problems that shall be evaluated and corrected before any samples are processed for the analytes of interest.

**Table 6-5. Analytical Requirements for Volatile Quality Control
(Gas Chromatography/Mass Spectrometry).**

Quality Control Requirements	Frequency	Criteria	Corrective Action
Tune	Once on a 12-hour clock	See Section 4.0	Investigate. Correct.
Continuing calibration check	Once on a 12-hour clock	See Section 4.0 and Section 6.7.3	Investigate. Correct. Re-analyze.
Internal standard	Each sample, QC sample, blank, and standard	See Section 6.7.5	Re-analyze or re-prepare as appropriate.
Qualitative identification	Each sample	Compare to spectra generated and retention times	Report any unusual circumstances in narrative.
Quantitation	Each sample (see Section 4.0 for surrogate and internal standard)	Calculate off continuing calibration	Report any unusual circumstances in narrative.

**Table 6-6. Analytical Requirements for Semi-Volatile Quality Control
(Gas Chromatography/Mass Spectrometry).**

Quality Control Requirements	Frequency	Criteria	Corrective Action
Tune	Once on a 12-hour clock.	See Section 4.0	Investigate. Correct.
Continuing calibration check	Once on a 12-hour clock.	See Section 4.0 and Section 6.7.3	Investigate. Correct. Re-analyze.
Internal standard	Each sample, QC sample, blank, and standard.	See Section 6.7.5	Investigate. Correct and re-analyze or re-prepare.
Qualitative identification	Each sample.	Compare to spectra generated and retention times (Section 6.7.7)	Report any unusual circumstances in narrative.
Quantitation	Each sample. See also Section 4.0 for surrogate and internal standard.	Calculate off continuing calibration	Report any unusual circumstances in narrative.

Table 6-7. Analytical Requirements for Gas Chromatography.

Quality Control Requirements ^a	Frequency	Criteria	Corrective Action
CCV	Routinely during run according to method	As per method, evaluate for retention time and area response	Investigate. Correct. Re-analyze.
CCB	Routinely, following CCV according to method	Evaluate for carryover and contamination	Investigate. Correct. Re-analyze.

^a When using second column confirmation, all QC criteria are applicable to primary and secondary columns.

Table 6-8. Analytical Requirements for Total Carbon, Total Inorganic Carbon, and Total Organic Carbon Quality Control.

Quality Control Requirements	Frequency	Criteria	Corrective Action
CCV	Every 15 samples and at the end of the run	85 to 115%	Rerun previous 15 samples
CCB	After each CCV	< EQL	Rerun previous 15 samples

6.7.3 Continuing Calibration Verification

The CCV analytical standard is used to monitor instrument stability over time. Acceptable performance demonstrates the continued accuracy of the calibration. The CCV may be prepared from any reliable source. The ICV QC sample may be used as the CCV sample.

The calibration of organic analytical GC/MS methods is limited by analytical run time. Each run is defined by a 12-hour clock that cannot be exceeded. Each run starts with a CCV (after tuning). The analyst shall rely on internal standard and surrogate performance to ensure that the sample run ended in control. Corrective action, such as re-analysis of all samples demonstrating unacceptable internal standard performance, shall be taken.

Analytical runs for organic analysis (e.g., GC) typically can extend from several hours to several days. Continuing calibration checks are required throughout the duration of the run (e.g., approximately every 10 samples for EPA SW-846 methods, every 12 hours for Contract Laboratory Program methods). Total organic carbon, total inorganic carbon, and total carbon measurements should also include CCV checks every 15 samples and at the end of the analytical run.

All samples analyzed after the last acceptable CCV (see Table 6-5 through Table 6-8) shall be re-analyzed. Re-analysis applies to specific analyte failure.

6.7.4 Continuing Calibration Blank

CCBs (i.e., instrument blanks) monitor effects such as contamination and instrument response drift. The CCB is a reagent blank prepared similarly to the standards but not subjected to preliminary sample preparation except for techniques in which the preparation is an integral part of the analysis (i.e., purge and trap procedures). In these cases, the preparation blank or method blank can be considered the equivalent of the ICB or CCB. The generally accepted criterion for reagent blanks is that they are below the EQL for each analyte tested. When an analyte exceeds this criterion, the analysis shall be investigated for potential impact. Samples with target analyte concentrations exceeding the blank contamination level by a factor of 20 or more can be reported unless client requirements dictate otherwise. In all other cases, all samples analyzed since the last acceptable ICB or CCB shall be re-analyzed for the specific analyte failure.

Several organic compounds are more readily introduced into blanks (Section 6.6.2 identifies specific compounds). In the case of organic analysis by GC/MS, the blank is typically the equivalent of the method blank. The method blank is run after the CCV standard. Periodic calibration blanks are not analyzed. In the case of organic analysis by GC and carbon analysis, periodic blanks are recommended following each CCV.

6.7.5 Internal Standards

An internal standard is an analyte that is similar to the analyte(s) of interest in chemical composition and analytical response, but is normally not expected to be found in the sample. Internal standards are added to every standard, blank, MS, MSD, and sample before analysis. Internal standards are used as the basis for quantitation of the analytes of interest.

Selecting appropriate internal standards shall be method- and compound-list specific because all results are normalized based on internal standard performance. Laboratory procedures shall specify acceptance criteria (see Volume 1, Section 4.0).

Internal standards are used in organic GC/MS analysis, although they may be appropriate to other types of analysis. Generally, area counts falling < 50 percent or > 200 percent of original area counts in the continuing calibration standard are considered unacceptable.

6.7.6 Low-Level Standard

The low-level standard is used to monitor instrument performance in the region near the EQL. When the low-level standard concentration is included in the instrument calibration, a separate low-level standard is not required. Low-level standards are not required for total organic carbon, total inorganic carbon, and total carbon.

6.7.7 Tentatively Identified Compounds

A project/program may specify criteria for determination of TICs. The following criteria are suggested for consideration when making a project/program specification or may be used in lieu of such specifications.

The library match for a TIC should be higher than 75 percent before this detailed evaluation is initiated. The method-specified tune criteria should be met. Special attention to the tune at low masses should be taken when evaluating volatile compounds. The concentration of a TIC should be greater than 10 percent of the nearest internal standard or estimated 5 nanograms on column injection, whichever is smaller. Early (injection peak) and late eluting peaks (column bleed and coeluting compounds) should have adequate background subtraction to permit use of these TIC criteria. If isotopic patterns are present, the mass ratios should agree with the reference spectrum within 10 percent. The base mass peak for the sample should be the same as the reference spectrum. If a molecular ion is present in the reference spectrum, the sample should also have a molecular ion mass. Reference spectrum ions greater than 20 percent should be in the sample spectrum. Sample ions greater than 20 percent that are not in the reference spectrum need to be evaluated. Major sample ions (greater than 20 percent) should match relative intensities to the base peak to those same ratios for the reference spectrum within 10 to 30 percent.

If a peak is determined to not meet the criteria for a TIC, the criteria for which it failed should be documented, so that it will not have to be evaluated again in the future.

A TIC compound may be upgraded to a positively identified compound (PIC). This is achieved by obtaining the compound, analyzing it under the same conditions as the initial identification, and matching retention time and mass spectrum. This may be done at the customer's request if they deem it necessary for the program.

6.8 PHYSICAL TESTING

Quality control specifications for several physical tests are provided in Table 6-9.

**Table 6-9. Physical Testing Quality Control
 (Differential Scanning Calorimetry, Thermogravimetric Analysis,
 and Differential Thermal Analysis/Thermogravimetric Analysis).**

Quality Control Requirements	Frequency	Criteria	Corrective Action
CCV (performance check) temperature characteristics	Each time the temperature ramp rate is changed	The standard(s) that is within the range of analysis and thermogravimetric analysis standard (material of known thermal properties) shall conform to known physical constants.	Investigate. Correct and restart. Recalibrate if necessary.
CCV (performance check) mass/weight characteristics	Periodically, at a minimum quarterly	Check balance performance using material of known mass or of known mass loss as a function of temperature properties.	Investigate. Correct. Restart. Recalibrate if necessary.

7.0 COMMON DATA QUALITY CALCULATIONS

This section provides various formulas that are typically employed to compute QC parameters that are used to assess data quality. These QC parameters should be monitored, evaluated, and/or trended on a short-term and long-term basis. For example, system contamination control (i.e., blank or background activity), precision, accuracy, spike recovery, tracer, or carrier yield recovery could be evaluated based on method, matrix, and activity or concentration level. These activities provide a basis for continuous quality improvement and insight on overall laboratory performance.

7.1 PRECISION

Precision is defined in Section 1.2.1. Sample precision is estimated by using duplicates, MSDs, or replicates. Samples used to calculate precision should contain concentrations of the analytes of interest above the MDC or EQL. The precision of a method in a given matrix is expressed as the RSD or the RPD.

In addition to precision as determined by the sample duplicate or MSD, precision for the standards (e.g., LCS, CCV standard) can be calculated and used to monitor QC of the analytical measurement system over time. Precision of the sample can also be monitored for long-term QC, but should be based on method, matrix, and activity/concentration in the sample.

7.1.1 Relative Standard Deviation

The RSD is used when at least three replicate measurements are performed on a given technique. The RSD is computed using the following equation:

$$\text{RSD} = \frac{s}{\bar{x}} * 100 \quad (7-1)$$

Where:

- s = Standard deviation with n - 1 degree of freedom
- n = Total number of observed values
- \bar{x} = Mean of observed values.

7.1.2 Relative Percent Difference

The RPD is used when two measurements exist. The RPD is generally used to express the precision of duplicate or spike duplicate samples. The RPD is computed using the following equation:

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} * 100 \quad (7-2)$$

Where:

- $x_{1,2}$ = Observed values
- \bar{x} = Mean of observed values.

7.2 ACCURACY

7.2.1 Method Accuracy Based on Sample Spike

Accuracy has been defined in Section 1.2.2. Accuracy for the sample is expressed as the percent recovery (%R) of a MS (or MSD) sample. The percent recovery is calculated based on the following equation:

$$\% R = \frac{(SSR - SR)}{SA} * 100 \quad (7-3)$$

Where:

- SSR = Spiked sample result
- SR = Sample result
- SA = Spike added.

7.2.2 Method Accuracy Based on Standard

The accuracy of an analytical method is expressed as the percent recovery of a standard (%R). The percent recovery of a standard is calculated according to the following equation:

$$\% R = \frac{A_m}{A_k} * 100 \quad (7-4)$$

Where:

- A_m = Measured value of the standard analyte
 A_k = Known value of the standard analyte.

Method accuracy obtained from either a sample spike or from a standard can be used to monitor QC of the analytical measurement system over time. Sample accuracy should be tracked based on the method, matrix, and activity/concentration when it is used for long-term QC monitoring.

7.3 YIELD RECOVERY (RADIOCHEMISTRY ONLY)

Yield percent recovery (%Y) of a tracer or carrier in radiochemical analysis is a measure of the effectiveness of separation methods for some radionuclides. It is expressed as the percent recovery and is generally used to correct the analyte recovery in the sample for radiochemical analysis. Yield percent recovery is calculated according to the following equation:

$$\% Y = \frac{T_m}{T_k} * 100 \quad (7-5)$$

Where:

- T_m = Measured value of the tracer or carrier
 T_k = Spiked known value of the tracer or carrier.

Yield percent recovery should be evaluated per procedure to monitor the effectiveness of the radionuclide separation. If tracer or carrier is not used on every sample, a historic yield percent recovery should be used as the correction factor for the sample analyte.

7.4 MEASURES OF AGREEMENT

7.4.1 Percent Difference

The percent difference (%D) is often used to compare one reference point to another (e.g., average RF from initial calibration compared to RF from continuing calibration listed in Section 7.1.2). The percent difference is calculated using the following equation:

$$\% D = \frac{|I - C|}{I} * 100 \quad (7-6)$$

Where:

- I = Observed value used as the reference point
- C = Compared value.

7.4.2 Bias

Bias (B) is often used to measure the deviation of a measured value from a known value or accepted reference value. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of analyte of interest spiked into a sample. Thus, the bias caused by the matrix effects based on a MS is calculated using the following equation:

$$B = (X_s - X_u) - K \quad (7-7)$$

Where:

- X_s = Measured value (e.g., spiked sample)
- X_u = Miscellaneous contribution (e.g., sample contribution)
- K = Known value (e.g., true spiked value).

If no miscellaneous contributions exist, X_u would be zero.

7.4.3 Mean Difference

Mean difference may be used to compare two duplicate results and is generally used for radiochemical analysis. The mean difference takes into account the uncertainty associated with each measurement. The mean difference is compared based on a two-sided z-test for a known population (*Principles and Procedures of Statistics* [Steel and Torrie 1960]) and is calculated using the following equation:

$$MD = \frac{|R_1 - R_2|}{\sqrt{(a_1^2 + a_2^2)}} \quad (7-8)$$

Where:

- R_1 = First sample result
- R_2 = Second sample result
- a_1 = One sigma uncertainty of first result
- a_2 = One sigma uncertainty of second result.

If the MD is greater than or equal to 1.96, a 95 percent confidence exists that the two results are not equal. If the MD is greater than or equal to 3, then there is a 99 percent confidence that results are not equal. The MD calculation is also referred to as relative error ratio or duplicate error ratio.

7.5 DETECTION LIMIT CONSIDERATIONS

A variety of definitions and protocols relating to detection and quantitation limits may be found in the literature, used by laboratories, or defined by government agencies. Unfortunately, universally accepted definitions and procedures do not exist. This can be frustrating and confusing for data generators or users. The discussions and definitions below are not intended to resolve all confusion, but rather to define the meaning and use of these terms within the scope of HASQARD.

Detection limit determinations are performed to give the laboratory, and subsequently the data user, information regarding the reliability of low-level results reported. A variety of approaches may be used, each of which portrays method sensitivity differently. This section describes several typical approaches that may be considered generically appropriate for HASQARD work. Alternate approaches may be used but must be accepted by the clients using the results reported under that approach. Each laboratory shall have procedures that document which approach it employs and describe how the determination is applied (i.e., performed in sample matrix or performed using low-level standards) and the frequency of verification required.

7.5.1 Inorganic and Organic Methods

Minimum detection and quantitation limit determinations are performed to give the laboratory, and subsequently the data user, information regarding the reliability of low-level results reported. An important characteristic of expression of sensitivity is the difference between the detection limit (DL) and the quantitation limit (QL). HASQARD will use the following definitions for DL and QL:

- DL is the minimum level at which the presence of an analyte can be reliably concluded.
- QL is the minimum concentration of analyte that can be quantitatively determined with acceptable precision and bias.

For most instrumental measurement systems, there is a region where semi-quantitative data is generated around the DL and below the QL. In this region, detection of an analyte may be confirmed but quantification of the analyte is unreliable within the accuracy and precision guidelines of the measurement system. When an analyte is detected below the QL, and the presence of the analyte is confirmed by meeting the qualitative identification criteria for the analyte, the analyte can be reliably reported, but the amount of the analyte can only be estimated. If data is to be reported in this region, it must be done so with a qualification that denotes the semi-quantitative nature of the result.

All client data shall reflect all method dilution factors (e.g., dilution factors resulting from sample preparation). When detection of an analyte cannot be confirmed, it shall be reported as:

- Not detected
- A qualified (flagged to indicate non-detection) numerical value, or
- Less than the detection limit.

These are based on client specifications or agreements with the laboratory.

7.5.1.1 Detection Limits

Numerous processes to estimate DLs for a specific analyte, matrix, or method exist, most of which involve spiking reagent water or other specific matrix with low concentrations of the analyte of interest followed by multiple analysis to allow statistical numerical evaluation of the data. Unfortunately, universally accepted procedures do not exist. The following subsections define several well-established processes that meet the intent of establishing DLs for HASQARD activities. Alternate approaches may be used but must be accepted by the clients using the results reported under that approach. Note also that some procedures explicitly specify how DLs shall be generated. In those cases, when those methods are identified to be run without modification (e.g., required by a permit), those methods will be considered acceptable.

7.5.1.1.1 Method Detection Limit

MDLs are determined in accordance with 40 CFR Part 136, Appendix B. Use of “MDL” will be only applicable to determinations derived from the 40 CFR 136, Appendix B reference. The MDL theoretically represents the concentration level for each analyte within a method at which the analyst is 99 percent confident that the true value is greater than zero. The MDL is determined for each analyte initially during the method validation process and updated as required in the analytical methods, whenever there is a significant change in the procedure or equipment, or based on project specific requirements. Reagent water MDLs can be described as “best case limits.” Detection limits achievable in clean samples may not be analytically achievable in other matrices.

7.5.1.1.2 Instrument Detection Limit

The IDL is sometimes used to assess the reasonableness of the MDLs, or in some cases required by the analytical method or program requirements. IDLs are most used in metals analyses but may be useful in demonstration of instrument performance in other areas. IDLs are calculated to determine an instrument’s sensitivity independent of any preparation method. Example methods to establish IDLs include:

- Using the average of standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven measurements per run (similar to MDL but without sample preparation) or

- Analysis of 10 instrument blanks and calculating three times the absolute value of the standard deviation.

If the determined IDL value is greater than the MDL, it may be used as the reported DL.

7.5.1.1.3 Non-Statistical Methods to Estimate Detection Limits

The concentration of the DL for the analyte of concern can be estimated by using one of the following approaches:

- Verification of detection over background or blank (as applicable), or
- An instrument signal-to-noise ratio of 2.5 to 5, or
- The region of a standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

7.5.1.2 Detection Limit Verification

Once the DL is determined (by whatever method employed by the laboratory), it must be verified on each instrument used for the given method. HASQARD defines the minimum detection limit verification (DLV) as the lowest concentration of a standard that is successfully verified.

DLV standards are extracted/digested and analyzed through the entire analytical process. DLV standards are generated by spiking a quality system matrix at approximately two to three times the DL (for a single-analyte standard) or approximately one to four times the DL (for a multi-analyte standard). DLVs are specific to each combination of analyte, matrix, method (including sample preparation), and instrument configuration.

DLV acceptance criteria shall be defined. The following identify typical (but not limited to) approaches:

- The apparent signal to noise ratio of the DLV must be at least three or adequate area count signals obtained, and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition) or
- For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations above the mean method blank concentrations.

Multiple instruments for a given method require a DLV on each instrument.

If the DLV fails, then the laboratory must redevelop their DL determination (with subsequent verification) or perform and pass two consecutive DLV verifications at a higher concentration and set the DLV at the higher concentration.

Periodic verification checks are required. Verification frequency shall be defined and is recommended to be annually at a minimum. So long as periodic checks are confirmed and there have been no technical or significant mechanical changes to the analytical equipment, no redeveloping of DL determinations are required (unless specifically defined by required protocol or permit).

Unless agreed to otherwise, when a numeric value is reported associated with a non-detected result, it shall be the DL value and flagged (e.g., “U” qualified). (DLV is approximately one to four times DL.)

DL and DLV determinations do not apply to methods that are not readily spiked (e.g., pH, turbidity, etc.) or where the laboratory does not report to the DL. Reporting of non-detected results in these circumstances shall be established between the laboratory and user before results are reported.

7.5.1.3 Quantitation Limits

There are several common approaches (or terminology used) that are used to establish QLs such as EQL, practical quantitation limit (PQL), or limit of quantitation. Unfortunately, universally accepted definitions for these do not exist.

The following are examples (but not limited to) of methods to establish these limits:

- A value 5 to 10 times MDL, however, it may be nominally chosen within these guidelines to simplify data reporting, or
- The lowest non-zero standard in the calibration curve, or
- The value established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point (from multi-point calibration scenarios) or the concentration of the low-level calibration check standard. Lower limits of quantitation are verified when all analytes in the lower limit of quantitation check sample are detected within ± 30 percent of their spiked value. This check should be used to both establish and confirm the lowest quantitation limit (e.g., EQL, PQL, or limit of quantitation [LOQ]). The lower limit of quantitation check sample is carried through the entire preparation and analytical procedure. This approach is generally used in metals analyses.

The laboratory must have procedures for establishing or verifying the QL values which must empirically demonstrate precision and bias. If the method is modified, precision and bias at the new QL must be demonstrated. Verification of QLs frequency shall be defined and is recommended to be annually at a minimum.

7.5.1.4 Reporting Limits

Reporting limits are included here because they are frequently used in lieu of detection/quantitation limits. The reporting limit may be statistically determined, may be an estimate that

is based upon the experience and judgment of the analyst, or based upon a nominal value to provide consistent results over time. Reporting limit values are generally defined to simplify data reporting and are frequently used for specific project reporting purposes. Reporting limit values cannot be lower than associated DLV values and are not typically lower than any established QLs (e.g., EQL, PQL, LOQ), but may be higher as agreed to between the laboratory and the client.

7.5.2 Radiochemistry Methods

The statistical nature of radionuclide decay coupled with the fact that the detectors used for analysis effectively determine (count) discrete decay events allows for a different approach to determining detection limits. Detection concepts are most frequently based on the probabilities for false positive (activity detected when not present) and/or false negative (activity not detected when actually present) limits. When at or near analytical detection levels for radionuclides, easily determined analytical counting errors become the predominant contributor to total analytical errors. Thus analytical precision can be evaluated even at the lowest reported result values. This eliminates the need for additional quantitation limit concepts and discussion for decay-based radionuclide analyses.

The calculations presented in the next two subsections are considered as *a priori* (i.e., before actual sample measurements). The calculation requires specification of nominal values of a number of parameters (e.g., background count rate, count time, known interferences, chemical recoveries, decay times). The true appropriate blank for a measurement process includes estimates of the nominal levels of any interference that may be present in a sample batch. In a number of situations, regulatory limits or contract specifications may require that the measurement process meet or exceed certain MDC limits for the sample batch of interest. Because these determinations require that some preliminary measurements be made, one finds that the assessment of *a priori* detection limit parameters for future measurements may require the knowledge of *a posteriori* (post measurement or alternate measurement) information concerning the nominal characteristics of the sample batch gained from preliminary measurements.

The question of whether the sample contains net activity is best answered by comparing the measurement result to the decision level or considering the confidence interval for the measurement result, not by comparing the result simply to the estimated MDA or MDC.

7.5.2.1 Decision Level Count Rate

The decision-level count rate (DLR) is defined as a 95 percent confidence limit for a critical decision level. This level is used for making a decision as to whether a sample emits radiation above the appropriate blank background level. The decision should be based solely on whether the net count rate observed for that sample exceeds this DLR. The DLR is calculated as shown below:

$$DLR = 1.645 * \sqrt{\frac{R_b}{T_b} + \frac{R_b}{T}} \quad (7-9)$$

Where:

- R_b = Background count rate
- T = Sample count time
- T_b = Background count time.

NOTE: *The DLR calculation referenced makes the assumption that the background count rate and the sample blank count rate are equal. Alternate DLR calculations can be used when they have been clearly defined and documented. The radio-analytical counting technique(s) where the alternate DLR calculations are applied shall also be identified.*

When T_b is assumed to be equal to T the DLR can be simplified as shown below:

$$DLR = 1.645 * (S_b) * \sqrt{2} \quad (7-10)$$

Where:

- S_b = Standard deviation of background (or appropriate blank) count rate for the counting time (T).

For the purpose of interpreting whether an individual sample measurement is different from its appropriate blank, it is recommended that the laboratory compare the net sample count rate with a DLR calculated using the sample specific “appropriate” blank. The “appropriate” blank should include measurement interferences from impurities (e.g., elevated Compton continuum, channel crosstalk from higher energy alpha particles measured by liquid scintillation) that are not typically known *a priori* or included in the nominal *a priori* DLR limit. This “true” decision level for the sample is different from the nominal *a priori* decision limit. For some measurement processes, the determination of the “true” appropriate blank for each sample may be impractical. However, every effort should be taken to properly assess the parameters of the appropriate blank.

7.5.2.2 Minimum Detectable Activity

The MDA has been defined as a level of activity that is practically achievable by a measurement system. The sample MDA generally is applied as the mean (expected) activity of samples having a 5 percent probability of escaping detection and 5 percent probability of false detection. The MDA is calculated based on Currie’s (“Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry” [Currie 1968]) formula and is simplified to the following two equations when the counting time in the sample is the same as in the background.

$$MDA = \left[\left(\frac{2.71}{T} \right) + (2 * DLR) \right] / K \quad (7-11)$$

or

$$MDA = \left[\left(\frac{2.71}{T} \right) + (4.65 * S_b) \right] / K \quad (7-12)$$

Where:

- T = Sample count time
- K = Detector CF (e.g., count rate/disintegration rate)
- S_b = Standard deviation of background count rate for the counting time (T).

When T_b is not equal to T, MDA is calculated as shown below.

$$MDA = \frac{\frac{2.71}{T} + 3.3 * \sqrt{\frac{R_b}{T} + \frac{R_b}{T_b}}}{\xi * b * k} \quad (7-13)$$

Where:

- R_b = Background count rate
- T_b = Background count time
- T = Sample count time
- ξ = Counting efficiency
- b = Abundance
- k = Conversion factor to convert to desired units.

The MDC is defined as the mean concentration of samples having a 5 percent probability of escaping detection and 5 percent probability of false detection.

$$MDC = \frac{MDA}{q * Y * \text{decay}} \quad (7-14)$$

Where:

- q = sample quantity (e.g., g or ml)
Y = Chemical Yield
decay = decay factor (correction for radioactive decay to reference date).

Software provided by vendors may have variations of the above formula. A vendor-provided software or data reduction package is adequate for data calculation.

7.5.2.3 *A Priori* and *A Posteriori* Concepts and Information

DLR, MDA, and MDC are considered as *a priori* (i.e., before the measurement). The estimation of these quantities requires specification of nominal values of a number of parameters (e.g., background count rate, count time, estimated interferences, chemical recoveries, decay times). The true appropriate blank for a measurement process includes estimates of the nominal levels of any interferences that may be present in a sample batch. In a number of situations, regulatory limits or contract specifications may require that the measurement process meet or exceed certain MDC limits for the sample batch of interest. Because these determinations require that some preliminary measurements be made, one finds that the assessment of *a priori* detection limit parameters for future measurements may require the knowledge of *a posteriori* information concerning the nominal characteristics of the sample batch gained from preliminary measurements.

The question of whether the sample contains net activity is best answered by comparing the measurement result to the decision level or considering the confidence interval for the measurement result, not by comparing the result to the estimated MDA or MDC.

7.6 UNCERTAINTY

Laboratories shall document and apply procedures for estimating uncertainty and shall be consistent with ANSI/NCSS Z540.2-1997 (R2012), *U.S. Guide to the Expression of Uncertainty in Measurement*. The rigor associated with the protocol will depend on the relative contribution from each source of error. When a laboratory implements an industry-recognized method that already specifies the limits for major sources of uncertainty, the laboratory would meet this requirement providing it reported results consistent with the method. In such cases, the major sources of uncertainty would still be provided to the client (e.g., in terms of sample precision and accuracy results).

Uncertainty is expressed as the range of values in which the true value is estimated to lie. The uncertainty estimate consists of two components, systematic and random variability. Each contributing source of uncertainty is expected to be distributed over its range. Each systematic component can be estimated in terms of the measurement result for the contributing source of uncertainty. The analytical systematic component can be estimated using standard or spike recovery. The random analytical component can be estimated from replicate measurements of a sample. The total propagated uncertainty is calculated as the square root of the sum of the squares of random and systematic variabilities, as shown in the following equation. The

component of uncertainty has to be expressed in the same unit designation (e.g., concentration percentage).

$$\text{Total uncertainty} = \sqrt{(s_x^2) + \sum_{j=1}^q \delta_j^2} \quad (7-15)$$

Where:

- s_x = Standard error
- q = Number of systematic uncertainty component
- δ = Systematic uncertainties.

Uncertainty is commonly used in the radiochemical analyses to express method and counting error. The total random uncertainty is obtained by propagating the individual variance (s_i^2) and is expressed as the standard error based on multiple determinations of x . However, the typical radiochemical methods used are not sufficient to separate systematic and random uncertainties such that biases can be corrected. Uncertainty will be measured, or uncertainty will be estimated if it cannot be measured.

7.7 CONTROL CHARTS

Control charts provide the analyst with early warning of impending problems in a preparative or analytical method. Each laboratory shall document its policy regarding the use of control charts. The laboratory's policy shall articulate the manner in which control chart limits are established and revised and will further define how it will deal with statistical outliers. The criteria for selection and specification of statistical control limits shall be documented. Recommended limits should be 2σ for warning limits, 3σ for control limits. BS/LCS performance for all routine preparations shall be monitored via control charts. Radiochemical laboratories shall also monitor calibration verification standards (i.e., counter control standard for radiochemistry). In those cases where the analytical technique involves a large number of analytes (e.g., ICP, GC/MS) the laboratory may select a subset representative of the total for control charting. Additional information on the application, development, and use of control charts can be found in Washington State Department of Ecology's *Procedural Manual for the Environmental Laboratory Accreditation Program*. Tabulation of performance statistics can be used in lieu of a control chart.

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8.0 DATA ASSESSMENT AND VALIDATION

This section describes the data requirements and specifications between the laboratory and the client, allowing for successful data validation when required by a project or program. This section explains how data validation is integrated into the overall data assessment and DQO planning process. It is not meant to provide users with routine validation protocols; instead it provides guidance in the use of the tools to build an effective validation and assessment protocol based on the DQRs for a specific client-directed work activity.

8.1 DATA ASSESSMENT PROCESS

Data quality is assessed in two steps. The first step is data validation, traditionally an independent review of laboratory and field data to assure that the procedures, protocols, and client-specific requirements were correctly followed. The second step in the assessment process is a general data quality assessment. This includes a review to verify the following:

- Assumptions made during the planning process were accurate
- Sampling and analytical variability identified in the DQO planning process was met
- Data makes sense
- Suitability of the data for making decisions.

In addition, the overall data assessment determines the following:

- Any anomalies in the data were addressed and that further sampling and analysis were performed to confirm or negate the anomaly
- If corrective actions or a new assessment strategy is required.

8.2 PLANNING CONSIDERATIONS

A common problem is that validation and assessment of data are planned “after the fact” or after the data are collected. This sometimes results in the deliverables from the sampling and laboratory analysis being insufficient (e.g., disorganized, inadequately documented) for complete assessment of the data. The cost of validating poorly planned and insufficient data reports will increase the original laboratory analysis costs.

The problem is compounded when methods other than the Contract Laboratory Program protocols are specified. The Contract Laboratory Program methods have published validation criteria, while the other methods do not. The QC differs between the various methods. For example, the most recent Contract Laboratory Program GC/MS method for semivolatile organic compounds requires that all compounds except five have minimum RFs, while the EPA SW-846 methods use four compounds to verify minimum response. This difference may be significant in the final outcome of the validation process for semivolatile organic compounds.

When non-Contract Laboratory Program methods are used, a qualified person shall write a validation procedure(s). The validation procedure needs to be flexible enough to be adapted to include criteria from the project data requirements. For example, the need to generate accurate data from a background sample is critical because many decisions shall be based on the results from that data. If one were using the EPA SW-846 GC/MS methods, modifying the method and the data validation criteria to ensure that all compounds determined exhibit minimal response in calibration may be appropriate. Once validation procedures are prepared, the procedure shall be provided to the laboratory, such that they know how the data will be evaluated.

Planning assures that the validation and assessment criteria are reflected in the methods used to collect and analyze the samples. This will ensure that any data flags or qualifications are based on the QC and not because of a lack of deliverables or inconsistency between validation requirements, deliverables, and methods.

Planning should also result in specification of methods, which are validation and assessment procedures that reflect the requirements generated during the DQO planning process. The DQO planning process generates the following: (1) the decision rules, (2) the level of uncertainty that the decision maker is willing to accept, and (3) the decisions that shall be made. The level of uncertainty shall dictate the amount of false positives and/or false negatives that the decision maker is willing to accept. This information shall be provided to the laboratory, validators, and data management staff before project initiation.

8.3 ASSESSMENT AND VALIDATION

The assessment and validation process should identify potential false positives and false negatives. Additionally, the DQO planning process should detail the analytes and the action levels for each media. The analytes and action levels drive the detection limits and, thus, the methods. The validation and assessment should reflect these requirements.

During the planning phase, the laboratory should receive the following information:

- Analyte(s) of interest
- Any analyte(s) driving risk assessment or the overall decision
- Matrices to be sampled
- Action or regulatory levels (thresholds)
- Level of uncertainty the decision makers will accept (e.g., false positives, false negatives, and confidence level)
- Precision and accuracy requirements
- Sample locations and site history

- Suspected or known contaminants, based on site history or previous data
- Number of samples for analysis by matrices and collection schedule
- Budget and resources
- Any method requirements specified by EPA or the Washington State Department of Ecology
- Data deliverables required, including electronic deliverables.

In response to the above information, the laboratory should provide the following information:

- Analyte(s) measured by method, including method number or name and revision date for each matrix
- Detection limits (organic and inorganic) or estimated MDAs (radiochemistry)
- Accuracy and precision in the matrix or a similar matrix in question
- Copies of the laboratory procedures used
- QC samples required by the laboratory, such as method blanks, MSs, and duplicates
- Sample volume, preservation, and container requirements
- Format in which the data will be presented, including electronic and hard copy.

An agreement should be reached between the analytical services provider and the client as to who shall validate the data, what data shall be validated, who shall write the validation procedure, and how the data shall be sent to the validator. The laboratory and the client should agree on the data format and the validation criteria before samples are collected.

Before beginning sample collection, the validator or the validator and the laboratory should document the validation procedure. A qualified laboratory representative should review the validation procedure to assure that the laboratory is capable of meeting the requirements specified. The following areas should be assessed in the validation procedure:

- Calibration
- Continuing calibration
- Method blanks, instrument blanks, and/or backgrounds
- Duplicates
- MSs and/or tracer or carrier yields
- LCSs
- Holding times
- Identification of analyte(s) of interest

- Verification of TIC (Section 6.7.7)
- Interferences
- Quantitation criteria
- Instrument performance and counter efficiency
- Criteria for validation of detection limits
- Criteria for accuracy and precision assessment.

For organic compound analyses, the following areas should be addressed in addition to the previously stated items:

- Surrogates (used to assess accuracy)
- Tuning (used for GC/MS only)
- Lower area limits for minimum detection
- Chromatograms showing manual integration of baselines and spectra (including TICs)
- Instrument carry-over between analytical runs.

Validation of ICP should include criteria for evaluating interelement correction factors and how interferences shall be validated.

Additionally, an agreed-upon format to present any trends, in the laboratory or corrective actions taken, that affect sample results, should be presented with the data for validation.

8.4 DATA USABILITY

Remember, data is usable if it meets the intended end-use as specified in the DQO process. However, many validation procedures do not address data use. Several important facts need to be understood about many validation and assessment procedures, including the following:

- Method deficiencies may be observed but may not result in data being qualified (i.e., flagged as estimated or rejected).
- Data may be qualified and still be usable.
- Many published validation procedures do not address all aspects of data review.

Examples of method deficiencies not qualified and the data being qualified but usable are presented.

8.4.1 Example 1 – Unqualified Method Deficiencies

Aqueous samples are submitted for analysis for semivolatile organic compounds by Contract Laboratory Program protocol. Two surrogate recoveries in the associated method blank are above the acceptance criteria. The laboratory neglects to re-extract and/or re-analyze the method blank. The associated samples did not contain reportable levels of semivolatile organic compounds and all surrogate recoveries in the samples are within the acceptable criteria.

Although the analysis is deficient with respect to the requirements, the data is not qualified and is considered usable.

Samples are submitted for VOC analysis by 624, 8260, or Contract Laboratory Program protocols. The laboratory inadvertently neglects to analyze a method blank. All other QC requirements are met and target analytes are not detected in any of the samples. Although this is a method deficiency, the data is not qualified. The only intent of a blank is to demonstrate that any detected analytes in project samples are native to the sample and not introduced by the laboratory. When target analytes are not detected, no analytical basis exists for a blank, provided all other QCs meet criteria.

8.4.2 Example 2 -- Data Qualified But Usable

A sample is analyzed for VOCs and one of the three surrogate recoveries is 1 percent below the acceptance criterion. Although the data is qualified, the magnitude of the qualification is relatively insignificant with respect to the many other variables impacting data quality. Accordingly, the data for this sample, although qualified, is usable.

A significant number of aqueous samples are analyzed for semivolatile organic compounds by Contract Laboratory Program. All of the samples and the associated field blanks and method blanks reveal levels of phthalate esters at 10 to 15 $\mu\text{g/L}$; all other QCs were met. The reported phthalate ester results in samples are qualified because of blank contamination. Although the results are qualified, the analysis for these phthalate esters is usable, provided it is stated that phthalates are not present in samples at concentrations greater than 15 $\mu\text{g/L}$.

Once both the laboratory procedures and the validation criteria are in agreement and are agreed on and documented by the laboratory, the validator, and the client, the samples are submitted for analysis. After analysis and submission of the data to the validator, the laboratory should respond to reasonable queries from the validator regarding the data. The queries and responses should be written.

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9.0 REFERENCES AND BIBLIOGRAPHY

[40 CFR 136](#), “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” Title 40, *Code of Federal Regulations*, Part 136, as amended.

ANSI N42.14, *Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radionuclides*, American National Standards Institute, New York, New York.

ANSI N42.15, *American National Standard Check Sources for the Verification of Liquid-Scintillation Counting Systems*, American National Standards Institute, New York, New York.

ANSI N42.22, *American National Standard Traceability of Radioactive Sources to NIST and Associated Instrument Quality Control*, American National Standards Institute, New York, New York.

ANSI N42.23, *American National Standard Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories*, American National Standards Institute, New York, New York.

ANSI N42.25, *American National Standard Calibration and Usage of Alpha/Beta Proportional Counters*, American National Standards Institute, New York, New York.

ANSI/NCSL Z540.2-1997 (R2012), *U.S. Guide to the Expression of Uncertainty in Measurement*, American National Standards Institute, New York, New York.

ASTM E-29, *Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications*, American Society for Testing and Materials, West Conshohocken, Pennsylvania.

ASTM D7282-06, *Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements*, American National Standards Institute, New York, New York.

Clean Water Act of 1977, 33 USC 1251, et seq.

Comprehensive Environmental Response, Compensation, and Liability Act of 1980, 42 USC 9601, et seq.

Currie, L. A., 1968, “Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry,” *Analytical Chemistry* 40(3):586-593.

[EPA SW-846](#), *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., as amended

Procedural Manual for the Environmental Laboratory Accreditation Program, Publication No. 10-03-048, 2010, Washington State Department of Ecology, Olympia, Washington.

Keith, L. H., 1991, *Environmental Sampling and Analysis, A Practical Guide*, Lewis Publishers, Chelsea, Michigan.

Resource Conservation and Recovery Act of 1976, 42 USC 6901, et seq.

Steel, R. G. D., and J. H. Torrie, 1960, *Principles and Procedures of Statistics*, McGraw Hill Inc., New York, New York.

APPENDIX A

SUMMARY OF THE DATA QUALITY OBJECTIVE PLANNING PROCESS

This appendix summarizes the DQO planning process. The DQO planning process is a formal method between the laboratory and the client that defines the analytical requirements based on the end-use of data. Participants in the DQO planning process typically include projects engineers, laboratory scientists, sampling and regulatory specialists, a representative of the regulatory community, and a DQO process specialist.

The DQO planning process empowers both clients (which are the data users) and the laboratories (which are the data suppliers) to take control of and resolve vexing issues in a stepwise fashion. The process brings together the clients and the laboratories. Further, the process allows laboratories to be active participants in solving the problems. During this process, the laboratory and the client decide what data shall be needed to make the decision, determine how the data shall be used, and decide the QC required.

The process consists of seven main steps.

1. Understand the context
2. State the question(s)
3. Define the potential answer(s)
4. Select the measure(s)
5. Set error tolerances
6. Establish decision rule(s)
7. Optimize the design.

Table A-1 outlines the steps in the process, the information needed for the DQO planning process, and the information that the laboratory should provide to support the planning process.

**Table A-1. Data Needed and Provided by the Laboratory
for the Data Quality Objective Planning Process.**

Step	Information Needed for the DQO Planning Process	Information Provided by Laboratory
Understand the context	<ul style="list-style-type: none"> • Situation or site history • Previous data 	N/A
State the question(s)	<ul style="list-style-type: none"> • Issues and problems • Any analytes related to the problems 	N/A
Define the potential answer(s)	Responses to each question	N/A
Select the measure(s)	<ul style="list-style-type: none"> • Analyte lists • Analytes of concern • Analytes driving risk • Measurement areas • Boundaries and areas to sample • Matrices • Action and regulatory levels 	<ul style="list-style-type: none"> • Justification for or against certain analytes • Fate and transport information • Difficulty of analysis • Analytes that serve as indicators for other constituents
Set error tolerances	<ul style="list-style-type: none"> • Allowable difference between the regulatory level and the actual value • Needed level of false negative, false positive, or confidence • Variability of the sample matrix 	<ul style="list-style-type: none"> • Methods potentially used • Estimates of the detection levels and variability of the methods
Establish decision rule(s)	The measurement, error tolerance, and decision information combined into logical statements or logic diagrams to allow the decision criteria to be established	N/A
Optimize the design	<ul style="list-style-type: none"> • Sample locations • Analytes to be measured • Action levels • Number of samples by matrix • Method requirements by regulation 	<ul style="list-style-type: none"> • Methods used to measure analytes • Method detection limits • Precision and accuracy by method and analyte • Quality control sample types and frequency required (e.g., method, field, equipment blanks, MSs, and duplicates) • Sample volume, preservatives, and container requirements

APPENDIX B

U.S. ENVIRONMENTAL PROTECTION AGENCY, CONSENSUS, AND U.S. DEPARTMENT OF ENERGY METHODS

B.1 U.S. ENVIRONMENTAL PROTECTION AGENCY

SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, as amended, U.S. Environmental Protection Agency, Washington, D.C.

Contract Laboratory Program and Statement of Work.

For copies of these documents, contact your regional EPA office.

- EPA-402-B-04-001A - C (Volumes I - III), 2004, *Multi-Agency Radiological Laboratory Analytical Protocols (Final)*, U.S. Environmental Protection Agency, Washington, D.C.
- EPA/600/4-79-020, 1983, *Methods for Chemical Analysis of Water and Wastes*, PB84-128677, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.
- 40 CFR 136, Appendix A, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," *U.S. Code of Federal Regulations*, as amended.
- EPA/600/4-88-039, 1991, *Methods for the Determination of Organic Compounds in Drinking Water*, PB91-231480 National Technical Information Service, Springfield, Virginia.

B.2 CONSENSUS

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater* (Standard Methods), American Public Health Association, 1015 15th NW, Washington, D.C. 20005

American Society for Testing and Materials (ASTM) methods.

B.3 U.S. DEPARTMENT OF ENERGY

DOE/EM-0089T, *DOE Methods for Evaluating Environmental and Waste Management Samples*, as amended, Pacific Northwest National Laboratory, Richland, Washington.

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